

Optical and electrical properties of deep level impurity centres

by
S. Braun

1972



DEPARTMENT
OF
SOLID STATE PHYSICS



INSTITUTIONEN FÖR FASTA TILLSTÄNDETS FYSIK
LUNDS TEKNISKA HÖGSKOLA-LUNDS UNIVERSITET
LUND-SWEDEN



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41545326_0016

OPTICAL AND ELECTRICAL PROPERTIES OF

DEEP LEVEL IMPURITY CENTRES

av

Stellan Braun

civ ing, Kr

Akademisk avhandling som för avläggande av teknologie
doktorsexamen vid tekniska fakulteten vid universitetet i Lund
kommer att offentligen försvaras å Fysiska institutionens
föreläsningssal B, onsdagen den 18 april 1973, kl 13.15.

Optical and electrical properties
of deep level impurity centres

by

S. Braun

Optical and electrical properties
of deep level impurity centres

by

S. Braun



OPTICAL AND ELECTRICAL PROPERTIES OF
DEEP LEVEL IMPURITY CENTRES

S Braun

Avhandling för doktorsexamen

OPTICAL AND ELECTRICAL PROPERTIES OF

DEEP LEVEL IMPURITY CENTRES

by

S Braun

Lund Institute of Technology, Department of Solid State Physics
Box 725, S-220 07 Lund 7, Sweden

The main interest in semiconductor physics has hitherto been the study of intrinsic properties and properties of shallow level impurities. Little work on deep level impurities has yet been performed. This may partly be due to the fact that deep impurity levels, in contrast to shallow, did not play a significant part in the basic development of the earliest semiconductor devices e g diodes, transistors and solar-cells. The technological task was rather to avoid all types of impurities and lattice defects that produce deep energy levels.

The need for more flexible devices has, however, demand an increasing degree of control over parameters such as diffusion length and lifetime. Important examples of such devices are fast silicon diodes, high sensitive photoconductors and light-emitting diodes. In spite of an increasing use of deep level impurities there is still very little information about such levels available, both experimentally and theoretically ¹⁾. To improve theoretical understanding of the properties of deep levels, more experimental results about physical properties such as binding energy, lattice relaxation effects, capture cross sections and emission rates are needed. The lack of experimental results is mostly due to the non-existence of good experimental methods.

From an experimental point of view, there are two fundamental properties which make investigations of impurity with deep levels more difficult than those with shallow levels. First, the solubility of an impurity decreases roughly as the fourth power of the binding energy. That means that whilst impurities with shallow levels, for example As, B and P,

can be doped to a density of 10^{21} cm^{-3} , impurities with deep levels such as Au, Cu, Fe and S can only be doped to a density of about 10^{16} - 10^{18} cm^{-3} ³⁾. Secondly, the large lattice strain leads to more localized wave functions with reduced optical and electrical cross sections.

The purpose of this thesis is therefore to develop experimental methods suitable for the examination of certain deep impurity levels. The investigation comprise the following papers.

- I. Optical properties of gold acceptor and donor in silicon
Preprint
- II. Field-independence of thermal emission rate in Au-doped silicon
Sol State Comm 11, 1457 (1972)
- III. Thermal and optical generation current in reverse-biased gold-doped silicon P^+N junctions without depletion approximation
J Appl Phys, June (1973)
- IV Photoionization of electrons and holes at oxygen donors in gallium phosphide
Sol State Comm 12, (1973)
- V. Photocapacitance measurements of the energy levels in ZnSe:Mn
phys stat sol (a) 14, 527 (1972)

All papers have been published together with H G Grimmeiss. In paper V J W Allen, St Andrews, Scotland, also was a co-author.

The first paper presents a simple and sensitive method for determination of the spectral dependence for the absolute value of photoionization cross sections for a multilevel impurity. The reason for the use of gold doped silicon was to extend the photocurrent method³⁾ developed earlier at our institute to a more complicated system involving two different levels and to derive useful information for a technological highly developed and widely used system⁴⁾.

The method is based on the photovoltaic effect caused by extrinsic illumination from two different light-sources. By a proper choice of the

intensity ratio and photon energy, it was shown that, at least near the threshold energy, all photoionization cross sections could be measured directly proportional to the measured photocurrent. This is in contrast to the method developed simultaneously by Sah and co-workers⁵⁾⁶⁾ at the university of Illinois. In their method, one single measurement gives two optical and two thermal emission rates via a rather complicated calculation involving two transient measurements. Their measurements were also made on gold-doped silicon but were restricted to the acceptor level, since the inclusion of donor levels makes the situation too complicated for analysis.

The measured spectral dependence seems to follow the theory of Lucovsky⁷⁾ (using a δ -function potential) rather than that of H B Bebb et al⁸⁾ (using a compromise between a coulomb- and a δ -function potential). The sum of the measured threshold energies was in excellent agreement with the bandgap energy showing no measurable Franck-Condon-shift. Due to the very high sensitivity of our measurements, we could also observe some structure near the threshold energy for excitations from the valence band into both the acceptor and the donor levels. This structure gives two different energy thresholds separated by about 0.05 eV which is close to the spin-orbit splitting of 0.044 eV for the valence band.

In papers II and III, an important parameter for all types of extrinsic two-step excitations was investigated, namely the generation region. It was shown that neither of the assumptions used earlier was fully valid. For example, Queisser et al⁹⁾⁸⁾ and Ryvkin et al¹⁰⁾⁴⁾ assumed that the generation region was the same for both extrinsic and intrinsic excitation. On the other hand, Sah et al⁶⁾ assumed that the generation region for extrinsic excitation was identical to the space-charge region. Due to this assumption, they found a rather strong field dependence for the thermal excitation of the gold acceptor level in silicon. In papers II and III, however, it is shown both theoretically and experimentally that the two-step excitation process is generated only in the inner part of the space charge region. Using this generation region, the field dependence found by Sah et al⁶⁾ was no longer observed.

In papers IV and V, the same measuring technique was used to determine the binding energy of deep impurity levels in two different light-emitting

materials. In paper IV, the temperature dependence of the threshold energies for the oxygen donor level in GaP was measured for temperatures between 90 and 410 K.

In agreement with R N Bhargava's ¹¹⁾ photoluminescence measurements, we found that the oxygen donor level follows the valence band for temperatures above 295 K. But, in contrast to T N Morgan et al ¹²⁾, we found only a very small Franck-Condon shift. In paper V manganese-doped ZnSe-diodes were investigated. This is a rather new material for light emitting diodes with a nearly "white" colour: it is therefore more favourable for the eyes than the red light-emitting GaP-diodes. The light is emitted from recombination processes involving manganese levels. Hitherto, there had been no information whatsoever available about the binding energy and the position in the forbidden energy gap for the manganese level. Since so far only n-type ZnSe has been obtained, the diodes have had to be in the form of Schottky barriers. The most convenient way to get a rough estimate of the position of the energy level was therefore to make a differential capacitance measurement with two different light sources. With this method, the manganese level was determined to 2.0 eV below the conduction band and 0.65 eV above the valence band.

Acknowledgements

To professor H G Grimmeiss I would like to express my sincere thanks for a stimulating and encouraging collaboration and expert guidance into the mysteries of semiconductor physics.

To all members of the institute, my sincere thanks for your unfailing assistance, frequent reminders and good comradeship during the time this work was being carried out.

References

- 1) For a recent review, see H J Queisser, Festkörperprobleme XI, pp 45-64 (Pergamon Press 1971)
- 2) F A Trumbore, Bell System Tech J 39, 205 (1960)
- 3) G Björklund and H G Grimmeiss, Sol State Electronics 14, 589 (1971)
- 4) For a review of gold in silicon, see e g
W M Bullis, Sol State Electronics 9, 143 (1966)
- 5) C T Sah, L Forbes, L L Rosier and A F Tasch, Jr, Sol State Electron 13, 759 (1970)
- 6) A F Tasch, Jr and C T Sah, Phys Rev B 1, 800 (1970)
- 7) G Lucovsky, Sol State Comm 3, 299 (1965)
- 8) H B Bebb and R A Chapman, J Phys Chem Sol 28, 2087 (1967)
- 9) G Güttler and H J Queisser, Energy conversion 10, 51 (1970)
- 10) F M Berkovskii and S M Ryvkin, Sov Phys Sol State 4, 263 (1962)
- 11) R N Bhargava, J Appl Phys 41, 3698 (1970)
- 12) T N Morgan, M H Pilkuhn and M R Lorenz, IBM Research paper RC-1612 (1966)

Optical properties of gold acceptor and donor in silicon

by

S Braun and H G Grimmeiss

Lund Institute of Technology, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

I. Introduction

One of the most interesting problems which still remains in semiconductor physics is that of impurity states. In contrast to shallow impurity levels, deep level impurity centres are not yet adequately understood although they very often play a vital role in recombination processes and hence in determining minority carrier lifetimes. From the experimental point of view, a deep-lying impurity level is characterized by its position in the forbidden energy gap and its capture and emission rates for electrons and holes. Previously the position of energy levels were usually determined from the thermal activation energy of Hall-constant and conductivity measurements and are normally uncertain by several hundredth of electron-volts. Better methods therefore have had to be developed to obtain more detailed information about the physical properties of impurity states.

Two attempts, each of which generates an expression for the photo ionization cross section which may be compared with experimental results, have recently been made ^{1) 2)} to describe the ground-state wave function for a deep centre. In one of these studies, Lucovsky renormalizes a delta-function potential of amplitude adjusted to give the experimentally observed ionization energy ¹⁾. Hence, by comparing experimental data with theoretical results, it should be possible to determine with high accuracy the energy E_T required to raise an electron thermally or optically from the top of the valence band into the unoccupied impurity level and the energy $E_C - E_T$ to raise

electrons from the occupied impurity level to the conduction band with its lowest energy at E_c . Furthermore, from the spectral distribution of the photo ionization cross section it might be possible to decide whether a deep centre can be described by a coulomb potential or more localized potential. Information such as this might be helpful in answering questions still open, e.g. as to how sharply the wave functions of deep impurity levels are localized and the possible significance of a strong electron-phonon coupling at deep centres. A few years ago, there was very little experimental information about emission rates of deep impurities available. Recently, however, several new methods have been developed ³⁾⁴⁾⁵⁾ to measure these qualities more accurately. In contrast to differential methods such as measurements of photocapacitance ³⁾, studies of steady state photocurrents with two light sources are especially suitable for the determination of threshold energies because they are directly proportional to the optical emission rate.

The purpose of this paper is therefore to report on the use of steady-state photocurrents to study the spectral distribution of the photo ionization cross sections in silicon doped with gold. All four photo ionization cross sections for the gold donor and acceptor level in silicon are measured in the same sample. For the first time absolute values for the hole emission from the gold donor level will be presented. Furthermore, it will be shown that the experimental results are in good agreement with Lucovsky's model ¹⁾ when the threshold energies, the only fitting parameters, are properly chosen and that the sum of the threshold energies is close to the bandgap E_g in the case of the gold acceptor. Gold-doped silicon has been used because gold creates two different energy levels in silicon which makes the analysis less straightforward. On the other hand, however, this system has been well investigated and is therefore especially suitable to test the applicability of this new method for the investigation of deep impurity levels.

II. Theoretical background

The experiments described in this paper make use of the impurity photovoltaic effect in reverse-biased P⁺N silicon junctions which are doped with gold impurities. Gold has an amphoteric behaviour in silicon and has an acceptor level at about 0.55 eV below the conduction band edge and a donor level about 0.35 eV above the valence band edge ⁶⁾ (fig 1). All measurements were performed below the freeze-out temperature of the gold impurity levels which means that thermal excitation process via these impurity levels could be neglected. In a previous paper ⁷⁾, it has been shown that the extrinsic photocurrent density of a reverse biased P-N junction illuminated with photons of energy $h\nu$ and intensity I is given by

$$J_R^0 = q(W - W_0) U \quad (1)$$

where U is the total net emission rate and W is the total space charge region of the junction. W_0 denotes the outer parts of the transition region in which the net excitation rate can be neglected because of competing recombination processes due to free carrier tails extending from the neutral regions into the space charge region.

In gold-doped silicon diodes there are three gold charge states. The total gold concentration is therefore given by

$$N_{Au} = N_1 + N_0 + N_{-1} \quad (2)$$

where N_1 , N_{-1} and N_0 are the concentrations of filled gold acceptor levels, empty gold donor levels and neutral gold impurity levels, respectively. The neutral impurity centres can be considered as being either filled donor levels or empty acceptor levels. From Shockley-Read-Hall statistics ⁸⁾⁹⁾ the concentrations of differently-charged gold impurities due to extrinsic illumination are readily calculated under steady state conditions in the region $W - W_0$ (fig 1) as

$$N_1 = N_{Au} \frac{e_{po}^o e_{p-1}^o}{e_{po}^o e_{p-1}^o + e_{n1}^o e_{no}^o + e_{p-1}^o e_{n1}^o} \quad (3)$$



$$N_o = N_{Au} \frac{e_{p-1}^o e_{nl}^o}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \quad (4)$$

$$N_{-1} = N_{Au} \frac{e_{nl}^o e_{no}^o}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \quad (5)$$

where $e_{nl}^o = \sigma_{nl}^o I$ and $e_{po}^o = \sigma_{po}^o I$ are the optical emission rates of electrons and holes for the acceptor level, respectively. Similarly, $e_{no}^o = \sigma_{no}^o I$ and $e_{p-1}^o = \sigma_{p-1}^o I$ are the optical emission rates of electrons and holes for the donor level, respectively. It follows from eqs (3), (4) and (5) that N_1 , N_o and N_{-1} are independent of intensity. The photocurrent J_R^o due to simultaneous excitation via the gold acceptor levels and gold donor levels is then given by the sum of two photocurrents created in their respective generation regions $W-W_o(a)$ for the acceptor levels and $W-W_o(d)$ for the donor levels:

$$J_R^o = q \left\{ e_{nl}^o N_1 [W-W_o(a)] + e_{no}^o N_o [W-W_o(d)] \right\} \quad (6)$$

In a previous paper ⁷⁾, it has been shown that the width of the region $W-W_o$ in which the photocurrent is generated depends on the energy position of the impurity level above the freeze-out temperature because $W-W_o$ is determined by the thermal emission rates of the impurity level at these temperatures. Below the freeze-out temperature, however, thermal excitation processes via the impurity level can be neglected and $W-W_o$ is determined by the optical emission rates. Hence, in the case of gold doped silicon, $W-W_o$ can be considered to be independent of the energy position of the impurity levels below 120°K and as equal for both the acceptor levels and the donor levels (equ 6 and 7 in ref 7). Inserting equ 3 and 4 in equ 6, we thus obtain for the extrinsic photocurrent density

$$J_R^o = q(W-W_o) N_{Au} \frac{e_{nl}^o e_{p-1}^o (e_{po}^o + e_{no}^o)}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \quad (7)$$

where $W-W_o$ depends on the reverse bias, the concentration of

$$N_o = N_{Au} \frac{e_{p-1}^o e_{nl}^o}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \quad (4)$$

$$N_{-1} = N_{Au} \frac{e_{nl}^o e_{no}^o}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \quad (5)$$

where $e_{nl}^o = \sigma_{nl}^o I$ and $e_{po}^o = \sigma_{po}^o I$ are the optical emission rates of electrons and holes for the acceptor level, respectively. Similarly, $e_{no}^o = \sigma_{no}^o I$ and $e_{p-1}^o = \sigma_{p-1}^o I$ are the optical emission rates of electrons and holes for the donor level, respectively. It follows from eqs (3), (4) and (5) that N_1 , N_o and N_{-1} are independent of intensity. The photocurrent J_R^o due to simultaneous excitation via the gold acceptor levels and gold donor levels is then given by the sum of two photocurrents created in their respective generation regions $W-W_o(a)$ for the acceptor levels and $W-W_o(d)$ for the donor levels:

$$J_R^o = q \left\{ e_{nl}^o N_1 [W-W_o(a)] + e_{no}^o N_o [W-W_o(d)] \right\} \quad (6)$$

In a previous paper ⁷⁾, it has been shown that the width of the region $W-W_o$ in which the photocurrent is generated depends on the energy position of the impurity level above the freeze-out temperature because $W-W_o$ is determined by the thermal emission rates of the impurity level at these temperatures. Below the freeze-out temperature, however, thermal excitation processes via the impurity level can be neglected and $W-W_o$ is determined by the optical emission rates. Hence, in the case of gold doped silicon, $W-W_o$ can be considered to be independent of the energy position of the impurity levels below 120°K and as equal for both the acceptor levels and the donor levels (equ 6 and 7 in ref 7). Inserting equ 3 and 4 in equ 6, we thus obtain for the extrinsic photocurrent density

$$J_R^o = q(W-W_o) N_{Au} \frac{e_{nl}^o e_{p-1}^o (e_{po}^o + e_{no}^o)}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \quad (7)$$

where $W-W_o$ depends on the reverse bias, the concentration of

$$N_o = N_{Au} \frac{e_{p-1}^o e_{n1}^o}{e_{po}^o e_{p-1}^o + e_{n1}^o e_{no}^o + e_{p-1}^o e_{n1}^o} \quad (4)$$

$$N_{-1} = N_{Au} \frac{e_{n1}^o e_{no}^o}{e_{po}^o e_{p-1}^o + e_{n1}^o e_{no}^o + e_{p-1}^o e_{n1}^o} \quad (5)$$

where $e_{n1}^o = \sigma_{n1}^o I$ and $e_{po}^o = \sigma_{po}^o I$ are the optical emission rates of electrons and holes for the acceptor level, respectively. Similarly, $e_{no}^o = \sigma_{no}^o I$ and $e_{p-1}^o = \sigma_{p-1}^o I$ are the optical emission rates of electrons and holes for the donor level, respectively. It follows from eqs (3), (4) and (5) that N_1 , N_o and N_{-1} are independent of intensity. The photocurrent J_R^o due to simultaneous excitation via the gold acceptor levels and gold donor levels is then given by the sum of two photocurrents created in their respective generation regions $W-W_o(a)$ for the acceptor levels and $W-W_o(d)$ for the donor levels:

$$J_R^o = q \left\{ e_{n1}^o N_1 [W-W_o(a)] + e_{no}^o N_o [W-W_o(d)] \right\} \quad (6)$$

In a previous paper ⁷⁾, it has been shown that the width of the region $W-W_o$ in which the photocurrent is generated depends on the energy position of the impurity level above the freeze-out temperature because $W-W_o$ is determined by the thermal emission rates of the impurity level at these temperatures. Below the freeze-out temperature, however, thermal excitation processes via the impurity level can be neglected and $W-W_o$ is determined by the optical emission rates. Hence, in the case of gold doped silicon, $W-W_o$ can be considered to be independent of the energy position of the impurity levels below 120°K and as equal for both the acceptor levels and the donor levels (equ 6 and 7 in ref 7). Inserting equ 3 and 4 in equ 6, we thus obtain for the extrinsic photocurrent density

$$J_R^o = q(W-W_o) N_{Au} \frac{e_{n1}^o e_{p-1}^o (e_{po}^o + e_{no}^o)}{e_{po}^o e_{p-1}^o + e_{n1}^o e_{no}^o + e_{p-1}^o e_{n1}^o} \quad (7)$$

where $W-W_o$ depends on the reverse bias, the concentration of

the shallow background doping and the degree of compensation due to the gold impurities ⁷⁾. A closer inspection of equ 7 shows that only doubtful information about the energy threshold for the excitation of electrons from the valence band into the gold acceptor can be obtained from the spectral distribution of the extrinsic photocurrent and that certainly no information about the other threshold energies and the optical emission rates is given. The reason for this is the change in occupancy when the photon energy is varied. Hence, in order to measure the energy dependence of optical emission rates from steady state photocurrents, the occupancy of the impurity levels has to be kept constant. This, however, is easily achieved by using a second light source with properly chosen constant photon energy $h\nu_s$ and high intensity I_s .

III. Experimental details

All measurements were performed on P^+N junctions where N is a lightly doped epitaxial layer with about $4-7 \cdot 10^{15}$ shallow donors/cm³, grown on the P^+ substrate with about $5-7 \cdot 10^{18}$ acceptors/cm³. The samples were gold-diffused between 890 °C and 960 °C giving a homogeneous gold impurity concentration between $0.5 \cdot 10^{15}$ cm⁻³ and $3 \cdot 10^{15}$ cm⁻³. The junctions were illuminated through the N region which was about 10 μ thick.

Because of the large difference between intrinsic and extrinsic absorption coefficients (fig 2), all kinds of stray light have to be avoided. As light sources, an incandescent lamp with a 0.75 m Jarrel-Ash Double Czerny-Turner scanning spectrometer or a Zeiss MM12 prism double monochromator was therefore used. In those cases in which a secondary light source was needed, a Bausch & Lomb high intensity grating monochromator was employed. A silicon or germanium filter was used to suppress stray light and higher orders of diffracted light. All current measurements have been performed with a Keithley electrometer 640 or a Keithley picoammeter 417 (with current suppression) in conjunction

with a Mosley strip card recorder 7101 BM. For capacitance measurements, a Boonton capacitancemeter 71 A was used and voltages were measured with a HP digital voltmeter type 3450 A.

IV. The optical emission rate e_{po}^O for hole emission from the gold acceptor level

When gold-doped silicon diodes are simultaneously illuminated with monochromatic light with constant energy $E_C - E_{Au^-} < h\nu_s < E_{Au^-} - E_V$ (i.e. $e_{pos}^O = 0$ and $e_{nos}^O = 0$) and intensity I_s such that

$$e_{p-ls}^O e_{nls}^O \gg e_{nls}^O (e_{no}^O + e_{p-l}^O) + e_{p-ls}^O (e_{po}^O + e_{nl}^O) \quad (8)$$

(i.e. $I \gg I_s$) the total photocurrent density calculated from equ 7 (see appendix) is given by

$$J_{Rh}^O = q(W - W_o) N_{Au} (e_{po}^O + e_{no}^O) = c_1 (e_{po}^O + e_{no}^O), \quad (9)$$

where c_1 can be considered as constant because $W - W_o$ is determined by the occupancy of the acceptor levels ⁷⁾ which is kept constant (i.e. zero) during the measurements according to (8).

Hence, for all photon energies less than $E_C - E_{Au^+} = 0.81$ eV (i.e. $e_{no}^O = 0$), the total photocurrent J_{Rh}^O is given by

$$J_{Rh}^O = q(W - W_o) N_{Au} e_{po}^O = c_1 e_{po}^O \quad (10)$$

The steady state photocurrent J_{Rh}^O is thus directly proportional to e_{po}^O . Measurements such as this provide therefore a unique and precise determination of threshold energies for the excitation of electrons from the valence band into the acceptor levels not influenced by competing absorption processes. They are only limited by the sensitivity of the amperemeter in contrast to differential methods such as measurements of photo capacitance. A further advantage using a second light source is that even diodes with high concentration of gold impurities can be investigated. Due to the constant occupancy, no changes in charge density occur within the transition region of the junction in

contrast to measurements with only one light source. Changes in $W-W_0$ and displacements currents therefore need not be taken into account. The spectral distribution of the relative photoionization cross section σ_{po}^0 obtained from steady-state photocurrents according to equ 10 is shown in fig 3.

V. Optical emission rate e_{nl}^0 for electron emission from the gold acceptor level

If the gold-doped silicon P^+N junctions are simultaneously illuminated with monochromatic light with constant energy $E_{Au-} - E_V < h\nu_s < E_C - E_{Au+}$ and intensity I_s such that all emission rates e_{jis}^0 (except e_{nos}^0 which is zero) are much larger than all emission rates e_{ji}^0 for variable photon energies, it can be shown (see appendix) that the increase in the photocurrent density $\Delta J_{Rl}^0 = J_{RT}^0 - J_R^0$ can be written as

$$\Delta J_{Rl}^0 = q(W-W_0) N_{Au} \left\{ b^2 e_{nl}^0 + (1-b)^2 e_{po}^0 + (1-b) \left(1-b \frac{e_{nls}^0}{e_{p-ls}^0} \right) e_{no}^0 \right\}, \quad (11)$$

where

$$b = N_l / N_{Au} \approx \frac{e_{pos}^0}{e_{pos}^0 + e_{nls}^0} \quad (12)$$

is the electron occupancy of the acceptor levels when the junction is illuminated with photons of energy $h\nu_s$ alone. For the above photon energy $h\nu_s < E_C - E_{Au+}$, equ 7 reduces to

$$J_R^0 = q(W-W_0) N_{Au} \frac{e_{nls}^0 e_{pos}^0}{e_{pos}^0 + e_{nls}^0} \quad (13)$$

Hence, by combining equ 10 and 13, b is readily obtained as

$$b = \frac{J_{Rh}^0 - J_R^0}{J_{Rh}^0} \quad (14)$$

For photon energies less than $E_C - E_{Au+} = 0.81$ eV (i.e. $e_{no}^0 = 0$), equ 11 can be rewritten and by using equ 10 we obtain:

$$\Delta J_{R\ell}^O - (1-b)^2 J_{Rh}^O = q(W-W_o) N_{Au} b^2 e_{nl}^O = c_1 b^2 e_{nl}^O = c_2 e_{nl}^O \quad (15)$$

where c_2 is again constant for constant photon energy $h\nu_s$. Measuring $\Delta J_{R\ell}^O - (1-b)^2 J_{Rh}^O$ as a function of photon energy thus provides precise information about the spectral dependence of the photo ionization cross section σ_{nl}^O even in the presence of competing absorption processes. J_{Rh}^O vanishes for photon energies less than $E_{Au-} - E_v = 0.61$ eV and the threshold energy for the excitation of electrons from the acceptor levels to the conduction band is therefore readily obtained from measurements of $\Delta J_{R\ell}^O$ alone.

For photon energies larger than $E_c - E_{Au+} = 0.81$ eV, excitation processes via the donor levels must be taken into account. This makes the analysis less straightforward. However, it will be shown later that e_{no}^O is rather small compared with the other emission rates and, hence, for gold-doped silicon, equ 15 is a good approximation even for larger photon energies. The spectral distribution of e_{nl}^O obtained from measurements of $\Delta J_{R\ell}^O$ according to equ 16 is shown in fig 3.

VI. The optical emission rate e_{p-1}^O for hole emission from the gold donor level

Using a photon energy $h\nu_s > E_c - E_{Au+}$ and intensities such that $e_{p-1s}^O \gg e_{p-1}^O$, the optically emission rate e_{p-1}^O for the excitation of electrons from the valence band into the gold donor levels can basically be measured analogous to e_{nl}^O . The expression for $\Delta J_{R\ell}^O$, which is more complicated than equ 15 in this case, reduces, however, appreciably when the variable photon energies are restricted to energies less than $E_c - E_{Au-} = 0.55$ eV (i.e. $e_{nl}^O = 0$, $e_{no}^O = 0$ and $e_{po}^O = 0$). Under these circumstances (see appendix), we obtain

$$\begin{aligned} \Delta J_{R\ell}^O &= q(W-W_o) N_{Au} e_{p-1}^O \frac{e_{nos}^O e_{nls}^{O2} (e_{pos}^O + e_{nos}^O)}{(e_{pos}^O e_{p-1s}^O + e_{nls}^O e_{nos}^O + e_{p-1s}^O e_{nls}^O)^2} \\ &= c_3 e_{p-1}^O \end{aligned} \quad (16)$$

where c_3 is constant for a constant photon energy $h\nu_s$. In chapter VII, it will be shown that e_{nos}^o is much smaller than the other optical emission rates. Hence, for the gold donor level in silicon, c_3 is very small and measurements of ΔJ_{Rl}^o are difficult to perform.

Instead, transient measurements have been used for the investigation of e_{p-1}^o . For this purpose, the gold donor (and acceptor) levels are emptied by illuminating the neutral N region with photon energies much larger than the band gap, which results in hole injection into the transition region. Next, the junction is illuminated with extrinsic photon energies $h\nu$ causing a transient photocurrent¹⁰⁾. For a three-state system, the transient is a sum of two exponentials with a faster and a slower time constant¹¹⁾. For the gold donor level in silicon, the expressions for the faster and slower time constant simplify to the form¹²⁾

$$\frac{1}{\tau_{fast}} = e_{p-1}^o \quad (17)$$

$$\frac{1}{\tau_{slow}} = e_{nl}^o + e_{po}^o \quad (18)$$

It is readily seen that for photon energies smaller than $E_{Au-} - E_v = 0.61$ eV (i.e. $e_{po}^o = e_{no}^o = 0$), there is only one time constant equal to $1/e_{p-1}^o$ because all acceptor levels are empty before illumination with photons of energy $h\nu$. In the energy range $E_{Au-} - E_v < h\nu < E_c - E_{Au+}$ the transient will be the sum of two exponentials where, however, $e_{p-1}^o = 1/\tau_{fast}$ in this case. Fig 4 shows the photocurrent decay at 0.62 eV (i.e. $h\nu \approx E_{Au-} - E_v$) and 0.69 eV (i.e. $h\nu > E_{Au-} - E_v$). The data given by the open circles are obtained by subtracting the slow photocurrent component from the transient observed with $h\nu = 0.69$ eV. The measured values for e_{p-1}^o are shown in fig 3 as a function of energy.

VII. The optical emission rate e_{no}^o for electron emission from the gold donor level

e_{no}^o is the most difficult emission rate in gold-doped silicon because one has to discriminate against the contribution of the three competing transition processes during the measurement. If the spectral distribution of e_{po}^o were known, the energy dependence of e_{no}^o could readily be obtained from measurements of J_{Rh}^o according to equ 10. Approximating the spectral distribution of e_{po}^o by Lucovsky's model ¹⁾ in this energy range, the energy dependence of e_{no}^o obtained from this procedure (fig 5) clearly shows a threshold energy at $E_C - E_{Au+}$. However, the absolute values are not in agreement with other experimental results. If e_{no}^o were as large as indicated in fig 5, measurements of ΔJ_{Rl}^o with photon energy $E_{Au+} - E_V < h\nu_s < E_C - E_{Au-}$ should give signals about one order of magnitude larger than those observed experimentally.

The optical emission rate e_{no}^o was therefore determined by measuring the occupancy of the gold donor levels after illuminating the junction with photon energies larger than $E_C - E_{Au+} \approx 0.8$ eV. The relative number of empty donor levels obtained is readily determined by integrating the transient photocurrent observed when the junction is subsequently illuminated with photons of energy $E_{Au+} - E_V < h\nu < E_C - E_{Au-}$. By comparing this charge with the integrated photocurrent observed when all donor levels are empty, the hole occupancy of the donor levels

$$b^+ = \frac{N_{-1}}{N_{Au}} \quad (19)$$

is readily obtained. Once again for these measurements no displacement current has to be considered and hence no information about the type of junction is needed. Inserting equ 5 in equ 19, we find

$$b^+ = \frac{e_{nl}^o e_{no}^o}{e_{po}^o e_{p-1}^o + e_{nl}^o e_{no}^o + e_{p-1}^o e_{nl}^o} \approx \frac{e_{nl}^o}{e_{p-1}^o (e_{po}^o + e_{nl}^o)} e_{no}^o \quad (20)$$

where we have taken into account that, from measurements of ΔJ_{Rl}^o ,

e_{no}^o is much smaller than the other emission rates. Consequently, measurements of e_{nl}^o , e_{po}^o and e_{p-1}^o are not very much influenced by electron emission from the donor levels for energies larger than $E_c - E_{Au+} = 0.81$ eV and can be used for estimating e_{no}^o using equ 20. Fig 3 shows the data for e_{no}^o as a function of energy obtained from the measured hole occupancy of the donor levels.

VIII. Absolute values of the photo ionization cross sections

From equ 20 it follows that e_{no}^o is correlated to e_{p-1}^o and the ratio e_{po}^o/e_{nl}^o . Whereas e_{po}^o/e_{nl}^o is readily determined from measurements of J_R^o and J_{Rh}^o according to eqs 12 and 14. From measurements of the transient photocurrent absolute values of e_{p-1}^o is obtained from equ 18. Hence, by measuring the intensities used for the excitation, absolute values for σ_{no}^o and σ_{p-1}^o are readily obtained. Moreover, the data found for σ_{no}^o are in agreement with these from $\Delta J_{R\ell}^o$ measurements. A similar procedure can be used for the determination of e_{po}^o and e_{nl}^o . Illuminating the junction with photons of energy $E_{Au-} - E_v < h\nu < E_c - E_{Au+}$ will partly empty the acceptor levels and occupy all donor levels. A transient photocurrent is therefore observed when the diode is subsequently illuminated with photons of energy $E_c - E_{Au-} < h\nu < E_{Au-} - E_v$. The time constant of this photocurrent is $1/e_{nl}^o$, giving the absolute value of σ_{nl}^o if the intensity used is known¹⁰⁾. Inserting e_{nl}^o in equ 12, σ_{po}^o is determined using equ 14. The spectral distributions for the absolute values of all four photo ionization cross sections are summarized in fig 6.

IX. Discussion

The theoretical expression obtained by Lucovsky for the energy dependence of the photo ionization cross section is

$$\sigma_i^o = \frac{1}{n} \left(\frac{F_{eff}}{F_o} \right)^2 \frac{16\pi q^2 \hbar}{3 m^*} \cdot \frac{E_i^{\frac{1}{2}} (h\nu - E_i)^{\frac{3}{2}}}{(h\nu)^3} \quad (21)$$

where n is the index of refraction, m^* is the effective mass, F_{eff}/F_0 the effective field ratio and E_1 is the energy threshold for the transition considered. Comparing the spectral distribution of the photo ionization cross section σ_{nl}^0 found experimentally with equ 21 (dotted line in fig 3), good agreement is obtained for energies smaller than 0.8 eV when E_1 is taken as 0.555 eV. For samples with low concentrations of gold impurities, good agreement with Lucovsky's model was found even for higher energies up to the band gap (fig 7). In these samples, however, an exponential tail was observed at small photon energies, σ_{nl}^0 being proportional to $\exp[-h\nu/(nkT)]$ down to about 10^{-20} cm^2 with $n \approx 1.25$. Nevertheless, for all concentrations, the best agreement with equ 21 was obtained with $E_1 = 0.555 \text{ eV}$.

A closer inspection of the energy dependence of σ_{po}^0 (fig 8) shows that there is a hump at small photon energies indicating at least two threshold energies. The data given by the open circles are obtained by subtracting equ 21 with $E_1' = 0.61 \text{ eV}$ (dotted line) from the experimentally found values for σ_{po}^0 . It is readily seen that these data are in excellent agreement with equ 21 for $E_1'' = 0.66 \text{ eV}$ (solid line).

Assuming, therefore, that the spectral distribution of σ_{po}^0 is due to the sum of two transitions with $E_1' = 0.61 \text{ eV}$ and $E_1'' = 0.66 \text{ eV}$ and that the probability for transitions with the larger threshold is three times larger than for the other transitions, excellent agreement between the experimental data for σ_{po}^0 and Lucovsky's model (dotted line for σ_{po}^0 in fig 3) is obtained.

A similar behaviour has not been observed for electron emissions. The shape of the σ_{po}^0 data should therefore arise from the valence band structure. Although the difference between the two threshold energies is about 50 meV, which is close to the spin-orbit-splitting of the valence band in silicon, more detailed calculations of optical cross sections including non-ideal band structures are needed for an unambiguous interpretation of the present experimental results.

Nevertheless, according to our interpretation a similar influence of the valence band structure on the spectral distribution of e_{p-1}^o might be expected. A closer inspection of the data for e_{p-1}^o once more yields a hump at small energies giving two threshold energies at 0.345 eV and 0.395 eV (fig 3). Again, with the assumption that the probability for the transitions with $E_1'' = 0.395$ eV is three times larger, excellent agreement is obtained with Lucovsky's model below about 0.52 eV (dotted line for σ_{p-1}^o in fig 3). Above this energy, the gold acceptor level, $E_C - E_{Au^-} = 0.555$ eV, becomes active. The difference between the experimental values and the dotted line for e_{p-1}^o at these energies in fig 3 can again be described by equ 21 if E_1 is taken as about 0.55 eV. As in the case of e_{po}^o , the absolute values are too large compared with the data for σ_{n1}^o obtained from steady-state photocurrents according to equ 15. No straightforward explanation for this behaviour can be given. However, because the deviation increases with an increasing degree of compensation by the gold impurities, one might think of phonon assistant transitions as being one of the possible reasons.

The otherwise good agreement of the experimental photo ionization cross sections with Lucovsky's model may, perhaps, indicate that the gold impurity levels in silicon can be described by sharply-localized wave functions. In addition, the sum of the threshold energies for the gold acceptor level (tab 1) is 1.165 eV which is very close to the band gap energy 1.161 eV at 90 °K. Activation energies obtained from the temperature dependence of the thermal emission rates e_n^t and e_p^t are in very good agreement with these values. Hence, we have to assume that relaxation effects are small.

The photo ionization cross section σ_{no}^o for electron emission from the neutral gold donor level was previously determined by Güttler and Queisser ¹⁴⁾ at room-temperature from measurements of J_R^o (fig 6). Because they used chopped light, uncertain value for the gold impurity density and apparently described the generation region by the minority carrier diffusion length,

their data for σ_{no}^0 are substantially different from ours. Recently, Tasch and Sah¹⁵⁾ investigated the parameters e_{nl}^0 and e_{po}^0 for electron and hole emission from the gold acceptor level, respectively, for energies below 0.85 eV using transient photocurrent measurements between 195 °K and 217 °K (fig 6). Their data differ only slightly from ours. In conclusion, we would like to mention that, from what has been said in chapter II, substantial errors might occur when optical measurements below the freeze-out temperature are combined with optical or electrical measurements above the freeze-out temperature due to different effective generation regions $W-W_0$.

X. Conclusion

All four photo ionization cross sections for electron and hole emission from the gold acceptor level and gold donor level in silicon have been evaluated in absolute values by junction photocurrents. Using two light sources, it has been shown that the impurity photovoltaic effect in the transition region of a semiconductor junction provides a unique determination of threshold energies for transitions between the energy bands and the impurity levels. The measurements are independent of the type of junction and the equations evaluated can be used for both linearly-graded and step junctions.

The experimental results are in good agreement with the δ -function impurity potential model of Lucovsky giving threshold energies of 0.555 eV and 0.61 eV for the electron and hole emission from the acceptor levels, respectively, and threshold energies of 0.75 - 0.83 eV and 0.345 eV for corresponding emissions from the donor levels. In the case of the acceptor levels, the sum of the threshold energies is very close to the band gap. It is therefore assumed that the gold impurity levels in silicon can be described by sharply localized wave-functions and that relaxation effects are very small.

Due to the high sensitivity of the measurements, the influence of the valence band structure on the energy dependence of the photo ionization cross section for the hole emission could also be investigated.

Acknowledgement

The authors would like to thank the Swedish Natural Science Research Council for their financial support.

APPENDIX

In a previous paper ⁷⁾, it has been shown that the reverse current density of a P-N junction illuminated with extrinsic light is given by

$$J_R^{o+t} = q(W-W_0) U \quad (A1)$$

where U is the total net emission rate and $W-W_0$ is the effective generation region within the transition region of the junction. From Shockley-Read-Hall statistics ⁸⁾⁹⁾, U is readily calculated for a single impurity level of concentration N_{TT} ⁷⁾ as

$$U = \frac{e_n^o e_p^o N_{TT}^2 + e_n^o N_{TT} p_1 / \tau_{po} + e_p^o N_{TT} n_1 / \tau_{no} + p_1 n_1 (1 - e^{-\frac{qV_R}{kT}}) / \tau_{no} \tau_{po}}{n_1 / \tau_{no} + p_1 / \tau_{po} + (e_n^o + e_p^o) N_{TT}} \quad (A2)$$

where $e_n^o = \sigma_n^o I$ and $e_p^o = \sigma_p^o I$ are the optical emission rates of electrons and holes, respectively. Otherwise the same notations as in ref 8 are used. Because the thermal emission rates of electrons e_n^t and holes e_p^t are equal to $n_1 / \tau_{no} N_{TT}$ and $p_1 / \tau_{po} N_{TT}$, respectively, equ A2 can be rewritten for $qV_R \gg kT$ as

$$U = N_{TT} \frac{e_n e_p}{e_n + e_p} \quad (A3)$$

where $e_n = e_n^o + e_n^t$ and $e_p = e_p^o + e_p^t$ are the combined emission rates for electrons and holes, respectively. For a three-state system such as gold impurities in silicon, the total occupancy

$$N_{TT} = N_1 + N_0 + N_{-1}$$

is fixed and the resultant net emission rate is therefore given (cf equ 7) by

$$U_T = N_{TT} \frac{e_{n1} e_{p-1} (e_{po} + e_{no})}{e_{n1} e_{no} + e_{po} e_{p-1} + e_{n1} e_{p-1}} \quad (A4)$$

Illuminating the junction simultaneously with two different photon energies $h\nu$ and $h\nu_s$ below the freeze-out temperature, the thermal emission rates can be neglected and we obtain for the

combined emission rates

$$e_{ni} = e_{ni}^o + e_{nis}^o \quad (A5)$$

$$e_{pi} = e_{pi}^o + e_{pis}^o \quad (A6)$$

where $i = 0, 1, -1$ and the subscript s denotes the optical emission rates for an energy $h\nu_s$. Inserting equ A4, A5 and A6 in equ A1, the total photocurrent density is given by

$$J_{RT}^o = q(W-W_o) N_{TT} \cdot \frac{(e_{nl}^o + e_{nls}^o)(e_{p-1}^o + e_{p-1s}^o)(e_{no}^o + e_{po}^o + e_{nos}^o + e_{pos}^o)}{(e_{nl}^o + e_{nls}^o)(e_{no}^o + e_{nos}^o) + (e_{po}^o + e_{pos}^o)(e_{p-1}^o + e_{p-1s}^o) + (e_{nl}^o + e_{nls}^o)(e_{p-1}^o + e_{p-1s}^o)} \quad (A7)$$

For $e_{nos}^o = e_{pos}^o = 0$ (i.e. $E_c - E_{Au-} < h\nu_s < E_{Au-} - E_v$) and $e_{nls}^o e_{p-1s}^o \gg (e_{no}^o + e_{p-1}^o) e_{nls}^o + (e_{po}^o + e_{nl}^o) e_{p-1s}^o$ (i.e. $I_s \gg J$), equ A7 reduces to equ 9.

The increase of the photocurrent due to the simultaneous illumination with photons of energy $h\nu$ is obtained by subtracting the photocurrent obtained with one light source of photon energy $h\nu_s$ according to equ A1 and A4 from the total photocurrent described by equ A7:

$$\Delta J_R^o = q(W-W_o) N_{TT} \cdot \left[\frac{(e_{nl}^o + e_{nls}^o)(e_{p-1}^o + e_{p-1s}^o)(e_{no}^o + e_{po}^o + e_{nos}^o + e_{pos}^o)}{(e_{nl}^o + e_{nls}^o)(e_{no}^o + e_{nos}^o) + (e_{po}^o + e_{pos}^o)(e_{p-1}^o + e_{p-1s}^o) + (e_{nl}^o + e_{nls}^o)(e_{p-1}^o + e_{p-1s}^o)} - \frac{e_{nls}^o e_{p-1s}^o (e_{pos}^o + e_{nos}^o)}{e_{nls}^o e_{nos}^o + e_{pos}^o e_{p-1s}^o + e_{nl}^o e_{p-1s}^o} \right] \quad (A8)$$

For $e_{nos}^o = 0$ (i.e. $E_{Au-} - E_v < h\nu_s < E_c - E_{Au+}$) and intensity I_s such that all e_{jis}^o (except e_{nos}^o) are much larger than all

e_{ji}^o (i e $I_s \gg I$), equ A8 simplifies to

$$\Delta J_{R\ell}^o = q(W-W_o)N_{TT} \left\{ e_{nl}^o \left(\frac{e_{pos}^o}{e_{nls}^o + e_{pos}^o} \right)^2 + e_{po}^o \left(\frac{e_{nls}^o}{e_{nls}^o + e_{pos}^o} \right)^2 + e_{no}^o \left[\frac{e_{nls}^o}{e_{nls}^o + e_{pos}^o} \left(1 - \frac{e_{nls}^o e_{pos}^o}{e_{p-1s}^o (e_{nls}^o + e_{pos}^o)} \right) \right] \right\} \quad (A9)$$

Inserting equ 12 in equ A9 we obtain equ 11. If, on the other hand, $e_{nl}^o = e_{no}^o = e_{po}^o = 0$ (i e $E_{Au^+} - E_v < h\nu < E_c - E_{Au^-}$), but $E_c - E_{Au^+} < h\nu_s < E_c - E_v$ and $e_{p-1s}^o \gg e_{p-1}^o$, equ A8 simplifies to equ 16.

REFERENCES

- 1) G Lucovsky, Sol State Comm 3, 299 (1965)
- 2) H B Bebb and R A Chapman, J Phys Chem Sol 28, 2087 (1967)
- 3) C T Sah, L Forbes, L L Rosier and A F Tasch, Jr,
Sol State Electron 13, 759 (1970)
- 4) L H Tang, J Appl Phys 42, 4101 (1970)
- 5) G Björklund and H G Grimmeiss, Sol State Electron 14, 589 (1971)
- 6) C B Collins, R O Carlson and C J Gallagher, Phys Rev 105,
1168 (1957)
- 7) S Braun and H G Grimmeiss, to be published in J Appl Phys,
June (1973)
- 8) W Shockley and W T Read, Jr, Phys Rev 87, 835 (1952)
- 9) R N Hall, Phys Rev 86, 600 (1952)
- 10) G Björklund and H G Grimmeiss, phys stat sol 42, K1 (1970)
- 11) H Kukimoto, C H Henry and F R Merritt, unpublished
- 12) From ref 11, where σ_{nj} is changed to σ_{nj-1} and σ_{pj} to
 σ_{pj-2} , the general expression for the time constant is
given by

$$\frac{1}{\tau} = \left(\frac{e_{p-1}^o + e_{po}^o + e_{nl}^o + e_{no}^o}{2} \right) + \left\{ \left(\frac{e_{p-1}^o + e_{no}^o + e_{po}^o - e_{nl}^o}{2} \right)^2 - e_{po}^o (e_{p-1}^o - e_{nl}^o) \right\}^{1/2}$$

which, for $e_{p-1} \gg e_{po}, e_{no}, e_{nl}$, gives equ 17 and 18.
- 13) O Engström and H G Grimmeiss, unpublished
- 14) G Güttler and H J Queisser, Energy conversion 10, 51 (1970)
- 15) A F Tasch, Jr, and C T Sah, Phys Rev B1, 800 (1970)

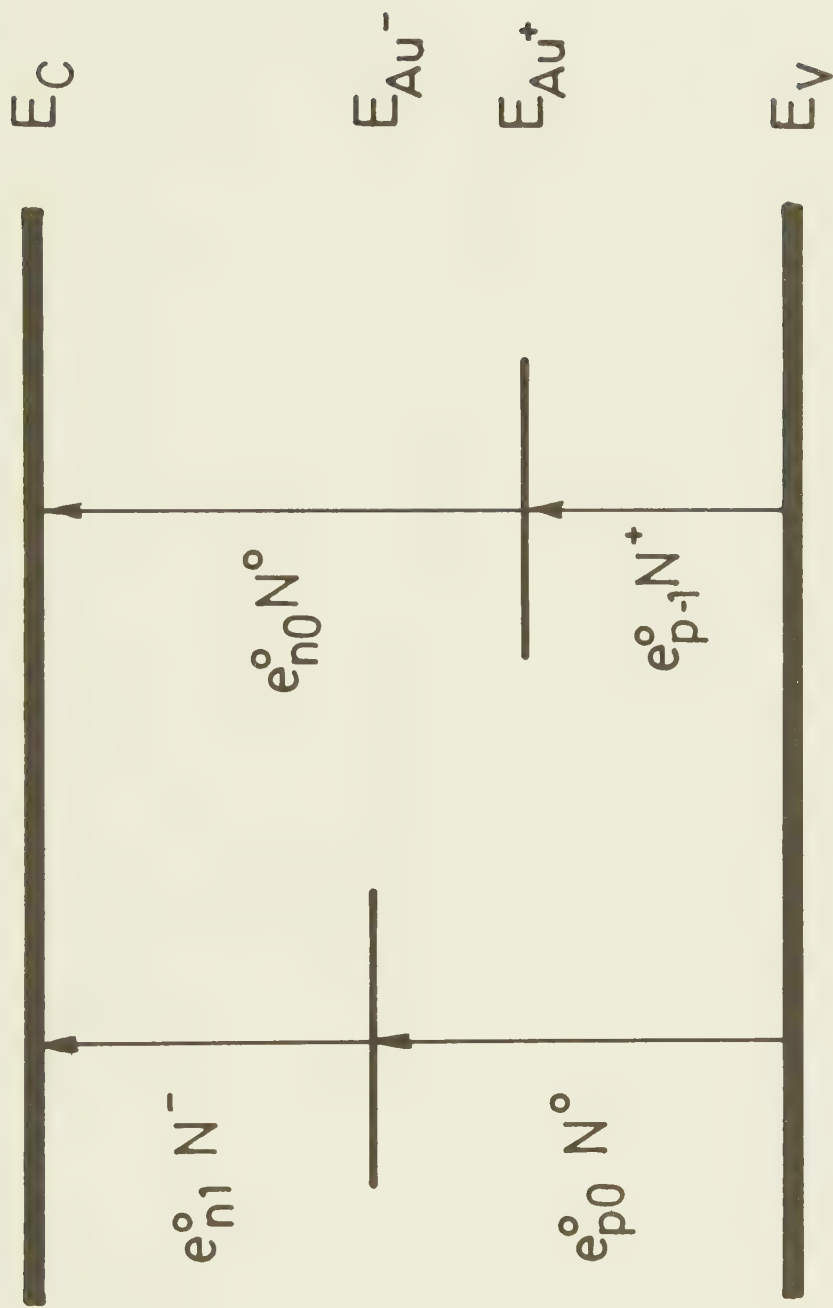
FIGURE CAPTIONS

- Fig 1 Energy level diagram and excitation processes during extrinsic illumination for gold in silicon.
- Fig 2 Typical short circuit current-curves for the structure used. *** with $3 \cdot 10^{15} \text{ cm}^{-3}$ gold impurities, ooo undoped diode.
- Fig 3 A plot of all four different photo ionization cross sections vs photon energy. The dotted lines are calculated from Lucovsky's model.
For σ_{p-1}^O and σ_{po}^O the dotted lines corresponds to the sum of two Lucovsky curves separated by 0.05 eV with the transition probability for the higher threshold being three times larger.
- Fig 4 Logarithm of the transient photocurrent vs time when both acceptor and donors were emptied (by hole injection $h\nu \gg E_g$) before the illumination started.
*** photon energy 0.62 eV only one time constant observed. ●●● photon energy 0.65 eV showing two different time constants. ooo the difference between the curve for the slow time constant and the measured points, giving the fast time constant.
- Fig 5 Plot of J_{Rh}^O vs photon energy with the σ_{po}^O -curve extrapolated according to Lucovsky's model (dotted line).
According to equ 10, the difference between J_{Rh}^O and σ_{po}^O (ooo) should directly give σ_{p-1}^O . The difference can again be described by a Lucovsky-curve giving a threshold of 0.81 eV, in good agreement with the energy $E_c - E_{Au+}$, but the absolute value is too large compared with more direct measurement as in fig 3.

- Fig 6 Absolute values of all four photo ionization cross sections for gold impurities in silicon at 90 °K. For comparison the results obtained by Tasch and Sah¹⁵⁾ for σ_{po}^o (curve 1) and σ_{nl}^o (curve 2) at 200 °K and by Güttler and Queisser¹⁴⁾ for σ_{p-1}^o at room-temperature are also given.
- Fig 7 σ_{nl}^o as calculated from equ 15 for a diode with low gold density ($5 \cdot 10^{14} \text{ cm}^{-3}$), showing good agreement with the Lucovsky-curve (dotted line) for energies up to the bandgap.
- Fig 8 Plot of σ_{po}^o vs for photon energies below 0.8 eV. The data given by the open circles are the differences between the measured points and the dotted Lucovsky-curve ($E_i = 0.61 \text{ eV}$). They can again be described by a Lucovsky-curve with a threshold energy of 0.66 eV and three times larger transition probability than for the lower threshold.

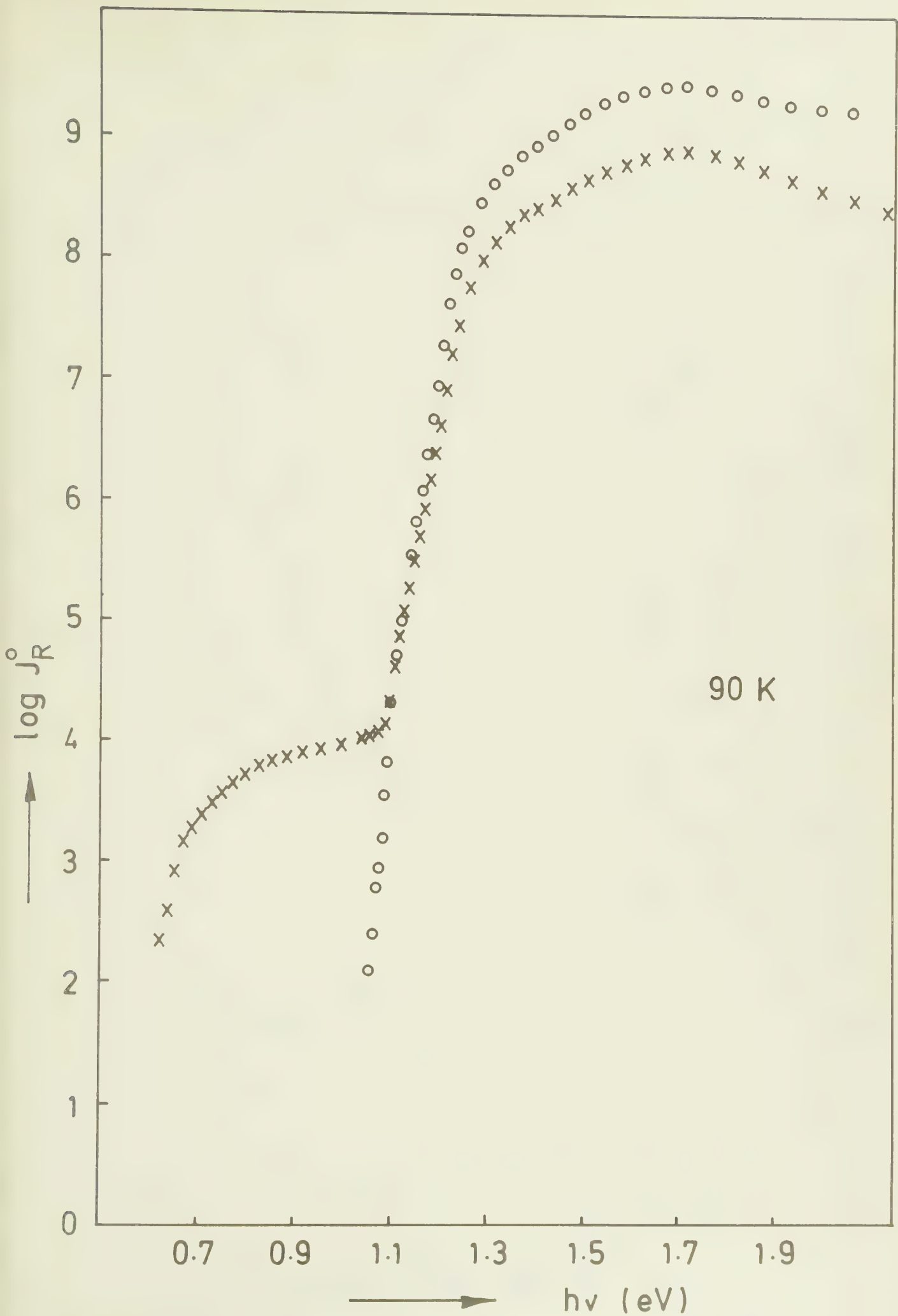
Table I

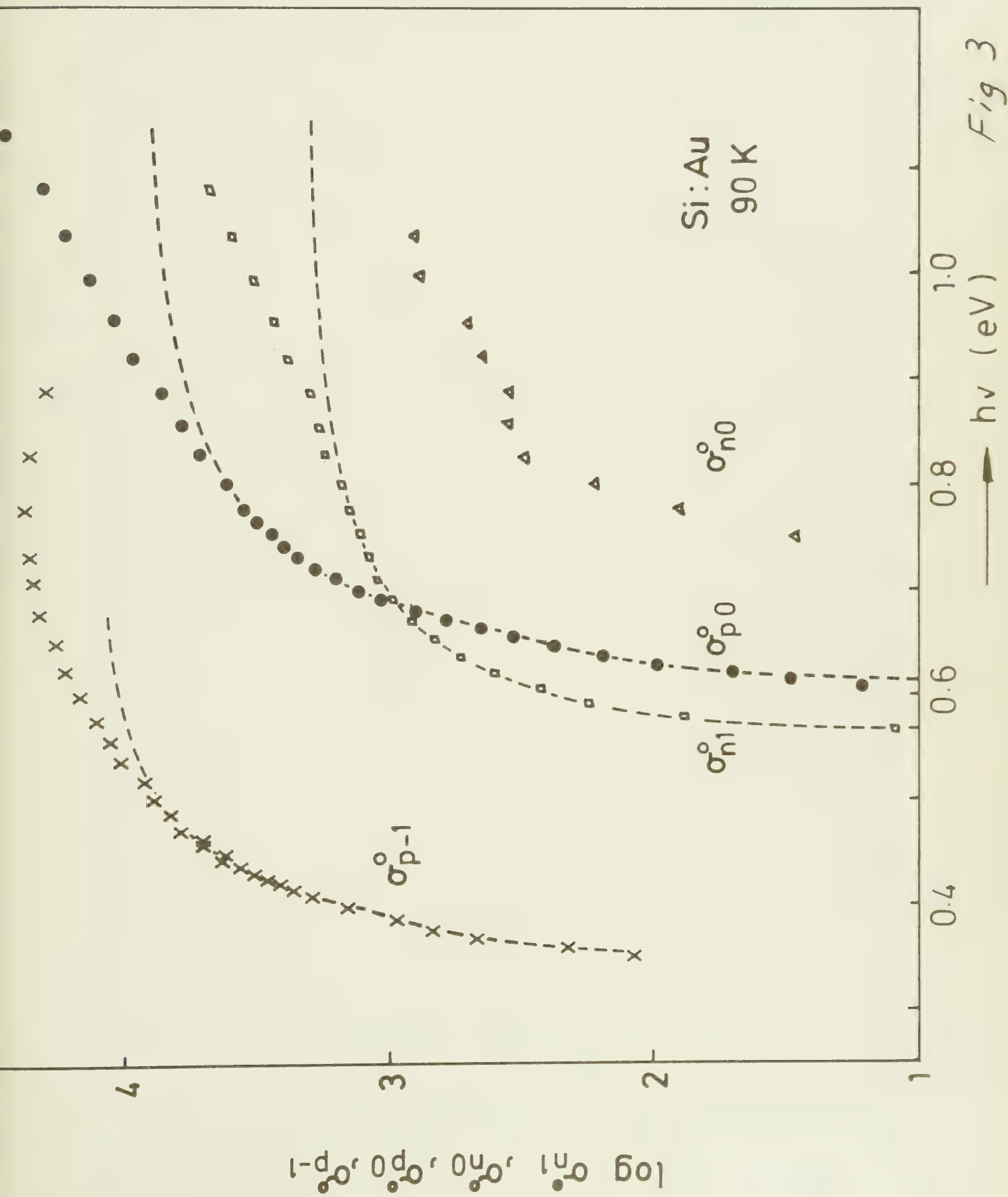
Photoionization cross section	threshold energy E_i (eV)
σ_{n1}°	0.555
σ_{p0}°	0.61
σ_{p-1}	0.345
σ_{n0}°	0.75 - 0.83



$$N_{Au} = N1^- + N^o + N1^+$$

Fig 1





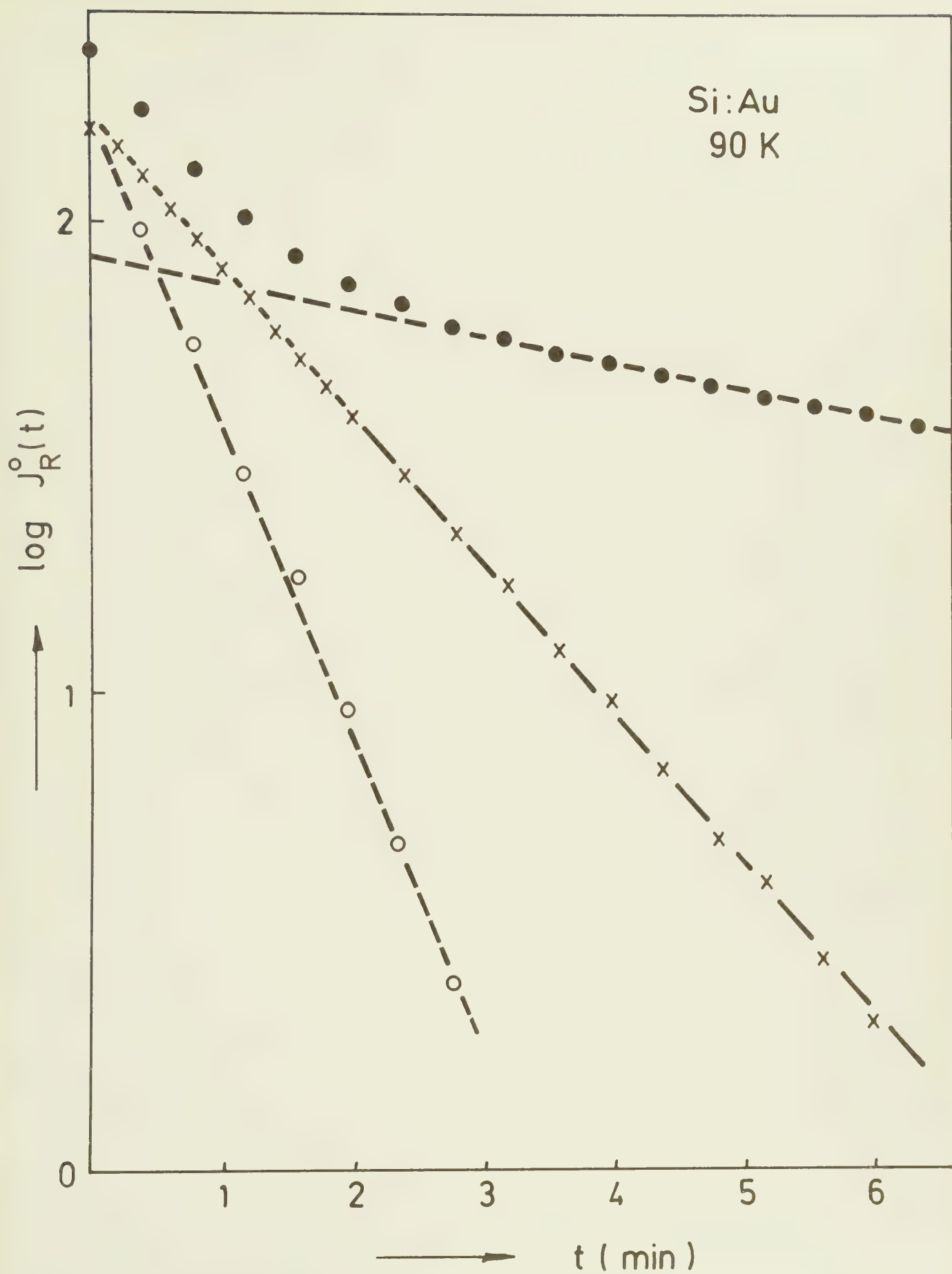


Fig 4

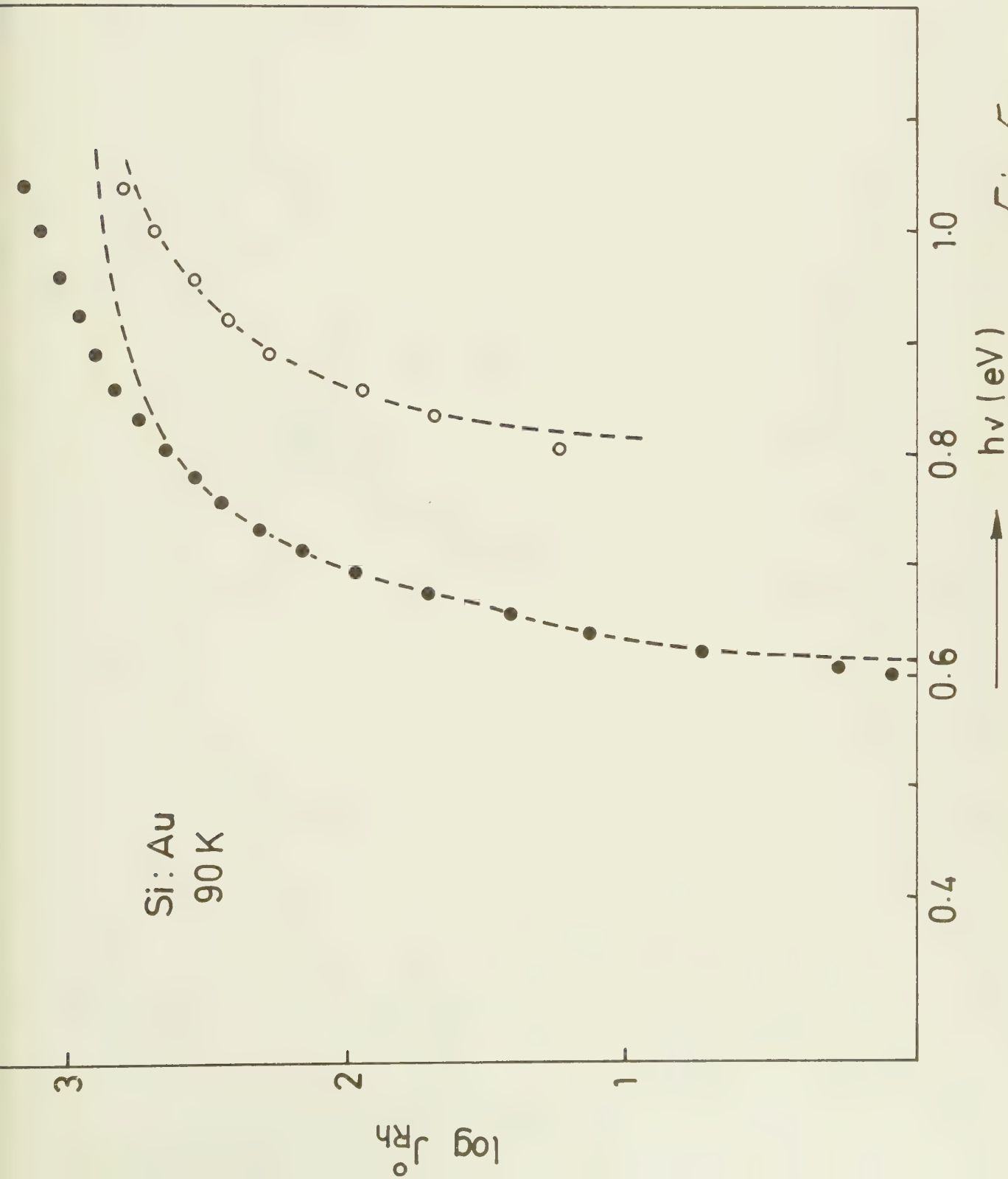
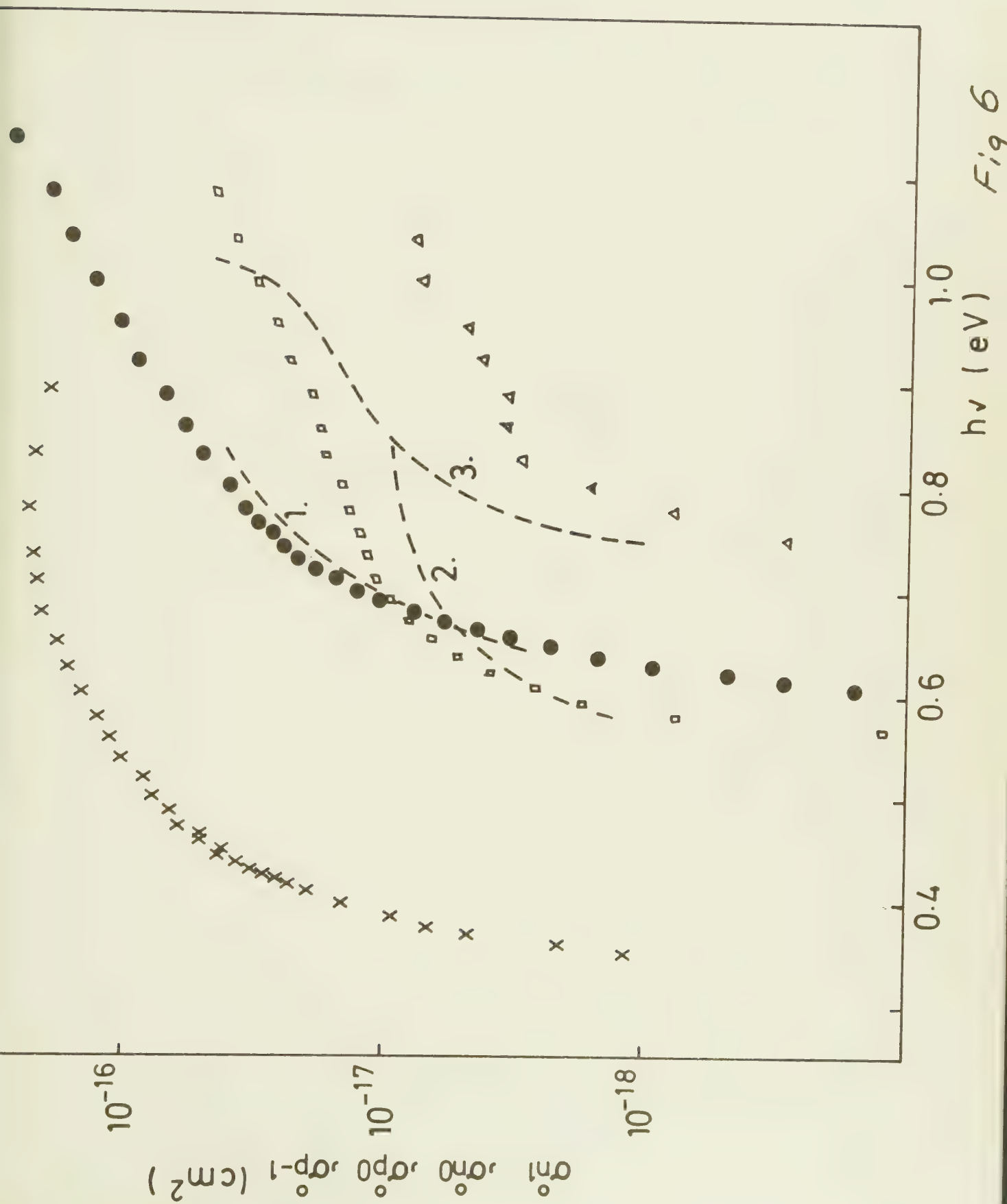


Fig 5



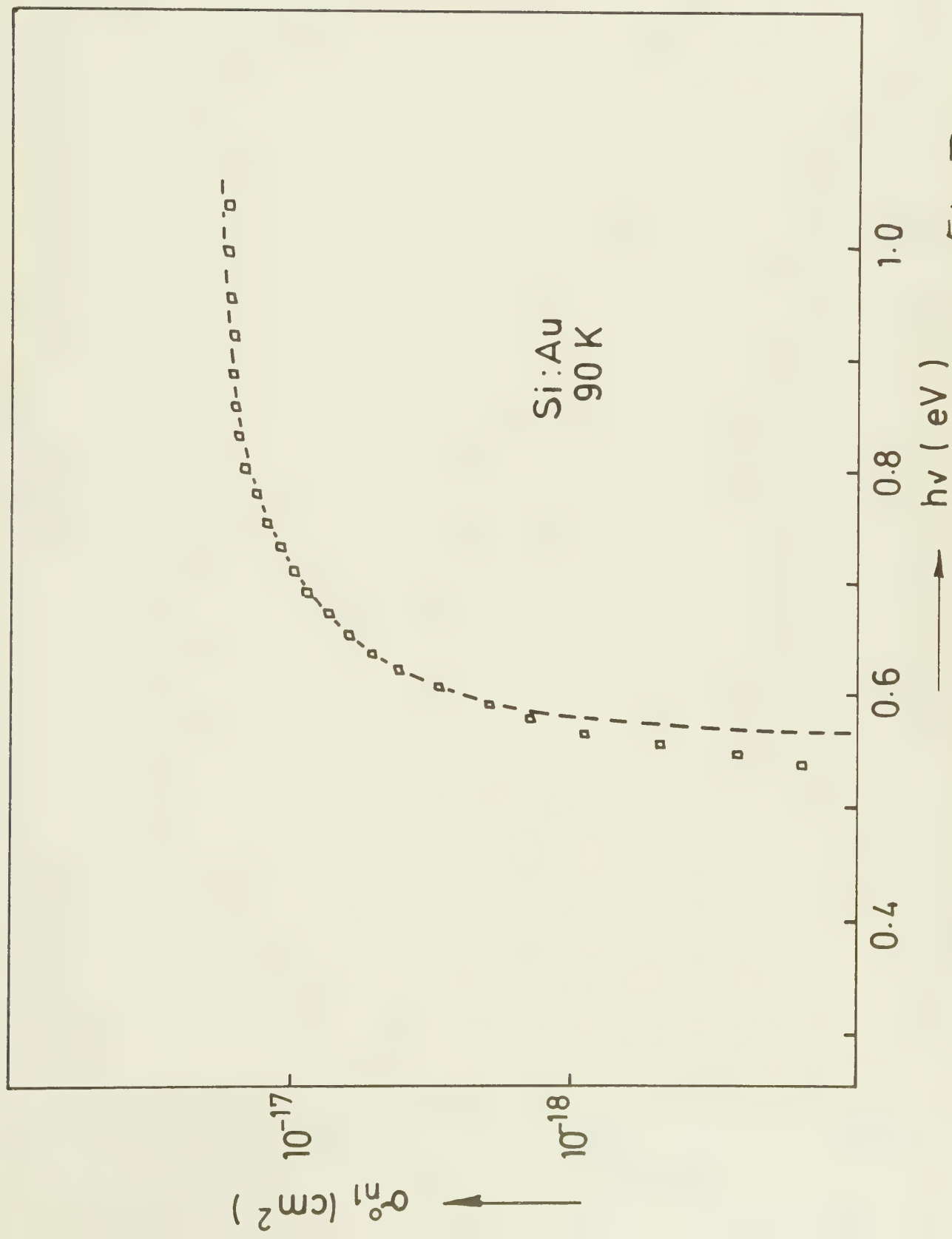


Fig 7

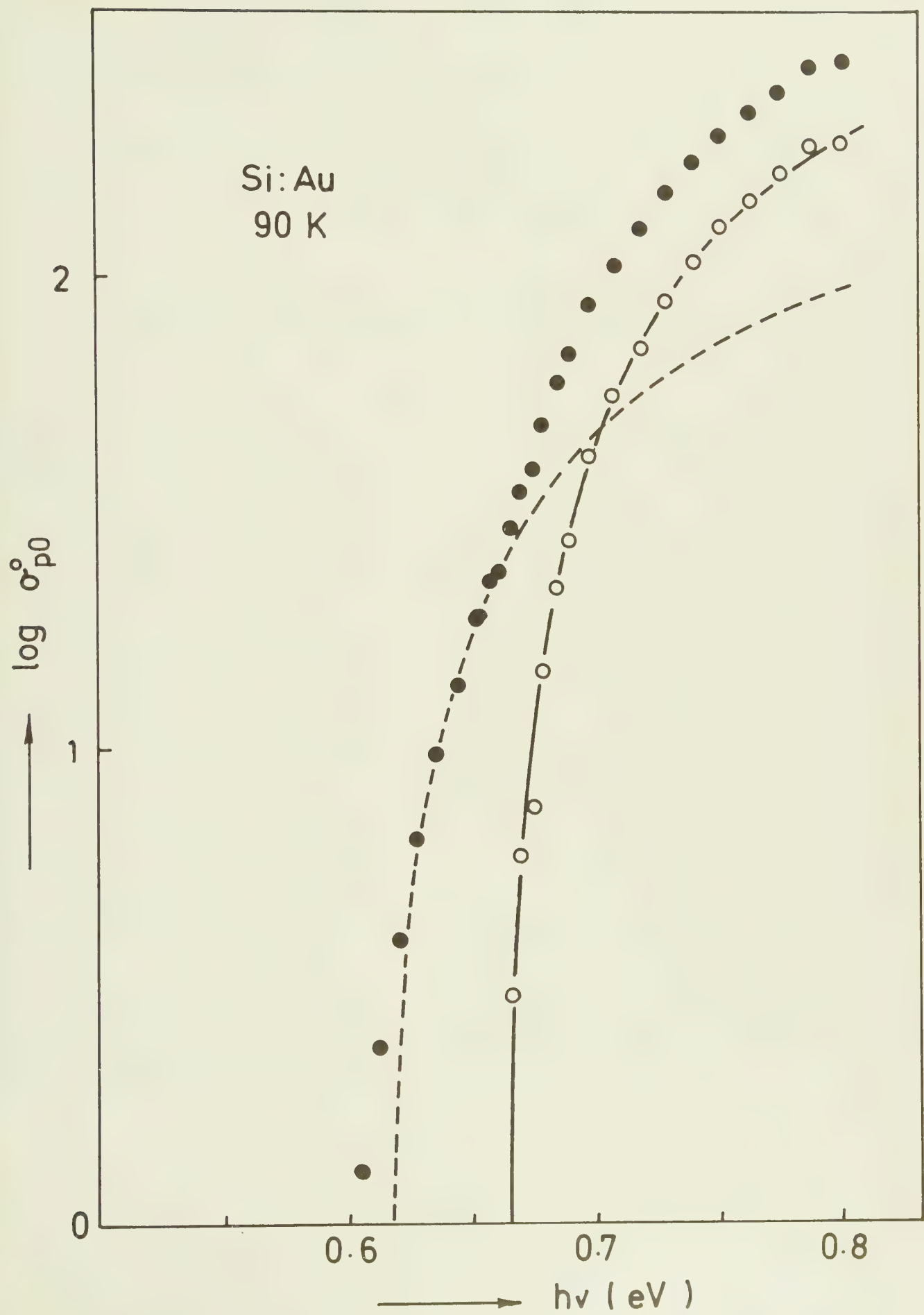


Fig. 8

FIELD-INDEPENDENCE OF THERMAL EMISSION RATE IN Au-DOPED SILICON

S. Braun and H.G. Grimmeiss

Department of Solid State Physics, The Lund Institute of Technology,
Box 725, S-220 07 Lund 7, Sweden

(Received 30 August 1972 by L. Hedin)

The thermal emission rate of holes, e_p^t , has been measured from dark leakage currents for the Au acceptor level in silicon diodes at different electric fields and found to be field independent for average electric fields below 10^5 V/cm.

DEEP impurities in semiconductors are not adequately understood¹ although they very often determine minority carrier lifetime and probably play a vital role in nonradiative recombination. In recent years, some new techniques have been developed²⁻⁴ for studying the fundamental physical properties of deep impurities. Very often these techniques make use of excitation processes via deep level impurity centres in reverse biased $P-N$ junctions. From these investigations can be deduced for instance thermal emission rates, thermal capture rates and photo ionization cross sections. However, these measurements involve fields of the order of 10^4 – 10^5 V/cm. The investigations are thus performed under conditions which are far from thermal equilibrium. It is therefore of great importance to know whether emission rates, capture rates and cross sections are field independent or not. The electric field dependences of thermal-emission rates have recently been investigated for fields below impact ionization by Tasch and Sah⁵ in Au doped Si, by Yau and Sah⁶ in Ag doped Si and by Rosier and Sah⁷ in S doped Si. In all three cases, a pronounced field-dependence of the thermal emission process via deep level impurity centres has been observed. These results have been obtained by assuming that under large reverse bias conditions the transition region of a $P-N$ junction is essentially depleted of mobile carriers and that all the space charge region W contributes to the dark leakage current density

which under these conditions is given by⁵

$$j_R = e N_{TT} \frac{e_n^t e_p^t}{e_n^t + e_p^t} W \quad (1)$$

where e is the electronic charge, N_{TT} is the impurity concentration of the deep level impurity, and e_n^t and e_p^t are the thermal emission rates of electrons and holes, respectively. Because in most cases one of the thermal emission rates is much larger than the other, the field-dependence of the thermal emission rates were observed by plotting j_R/W as a function of the average electric field.⁵ However, during measurements of optical emission rates in Au doped silicon,⁸ it has been found that due to free carrier tails the ends of the space charge region do not contribute to the dark leakage current. If this is true, the suppositions made for obtaining equation (1) are no longer valid and the field-dependence of the thermal emission rates of deep level impurities should be reconsidered. It is therefore the purpose of this paper to present the results of a study of the thermal emission rate e_p^t of Au acceptor levels in silicon measured at different electric fields. It will be shown that, within the experimental error, no field-dependence of e_p^t is observed for average electric fields below about 10^5 V/cm when recombination processes at the ends of the transition region are taken into account.

From detailed balance consideration, it is known⁹ that the net thermal excitation rate via an impurity centre in a semiconductor in the steady state is given by

$$U = \frac{g(V, T)}{(n_1 + n) \tau_{p0} + (p_1 + p) \tau_{n0}} \quad (2)$$

where n and p are the free electron and hole concentration respectively, n_1 and p_1 are given by $p_1 = n_i^2/n_1 = n_i \exp(E_i - E_t)/kT$, τ_{p0} is the lifetime for holes injected into highly n -type specimens, τ_{n0} is similarly the lifetime of electrons in a highly p -type sample and $g(V, T) = n_i^2 - np$. Assuming an exponential tail of free charge carriers extending from the neutral regions into the transition region, it is readily shown⁸ that in the space charge region of a reverse biased P - N junction $g(V, T)$ can be expressed as $n_i^2 [1 - \exp(-eV_R/kT)]$.

For the purpose of discussion, we will consider the case of a deep level located in the top half of the forbidden band-gap. The transition region W can then be divided into three distinct regions where the net rates of excitation are approximately given by $U_I = g(V, T)/p\tau_{n0}$, $U_{II} = g(V, T)/n_1\tau_{p0}$ and $U_{III} = g(V, T)/n\tau_{p0}$. The boundaries between these regions are defined by the conditions $p\tau_{n0} = n_1\tau_{p0}$ and $n = n_1$. Because n_1 is constant and smaller than p in region I and smaller than n in region III, we find $U_{II} > U_I$ and $U_{II} > U_{III}$. Thus the net thermal excitation process in the regions I and III can be neglected with respect to that in region II. Under large reverse bias conditions, the dark leakage current density of a P - N junction is therefore not adequately described by equation (1) but rather by a relation such as

$$j_R = e N_{TT} \frac{e_n^t e_p^t}{e_n^t + e_p^t} (W - W_0) \quad (3)$$

with W_0 corresponding to the width of regions I and III at the ends of the transition region where the net thermal excitation process can be neglected. For shallow impurities W_0 is normally small compared with W and equation (3) reduces to equation (1). The deeper, however, the impurity is the larger becomes W_0 and for impurity levels close to the middle of the forbidden bandgap (as for instance the Au acceptor level in silicon), W_0

will still be larger than half the transition region at fairly high reverse bias conditions. With increasing reverse bias, W_0 becomes rather voltage insensitive and can be considered as constant.¹⁰

At small reverse bias, however, W_0 will decrease with increasing V_R in non-symmetrical P - N junctions and the dark leakage current density j_R will no longer depend linearly on W . Because we assumed the deep-level impurity to be located in the top half of the forbidden band, the emission rate of electrons, e_n^t , will probably be much larger than the emission rate of holes, e_p^t . Equation (3) then reduces to

$$j_R = e N_{TT} e_p^t (W - W_0). \quad (4)$$

From equation (4), it is readily seen that a plot of the dark leakage current density against the total width W of the transition region should only give a straight line with slope $e N_{TT} e_p^t$ at large reverse bias if the thermal emission rate of holes, e_p^t , is field-independent. Measurements performed at 290°K on Au doped silicon P + N junctions clearly show (Fig. 1) that under large reverse bias conditions a straight line is obtained when the dark leakage current is plotted against W (which is $\sim 1/C$). Furthermore, extrapolating the straight line an intercept on the positive abscissa is observed and for small values of W (i.e. reverse bias) a deviation from the straight line is found due to the change in W_0 . Similar results have been obtained at 230°K. From this we conclude that e_p^t is field-independent for average electric fields about 10^5 V/cm.

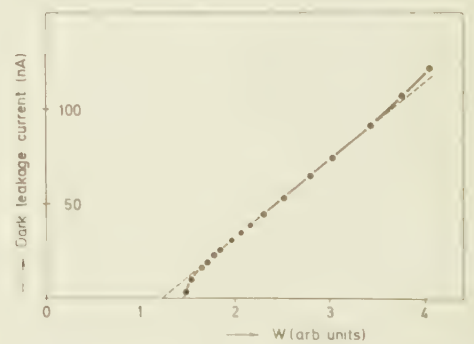


FIG. 1. Dark leakage current of an Au doped silicon P + N junction as a function of the total width W of the transition region at room temperature.

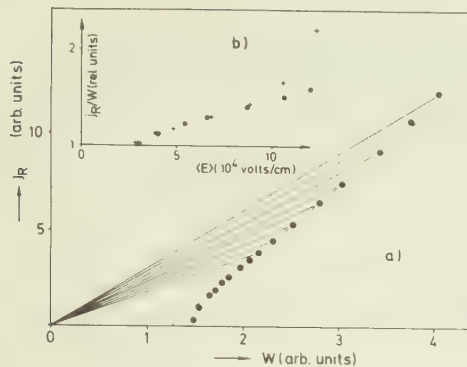


FIG. 2. (a) Dark leakage current density j_R as a function of the total width W of the transition region (see text). (b) j_R/W as a function of the average electric field, $\langle E \rangle = V_R/W$ (see text). ●● from Fig. 2(a), +++ from reference 5.

The field-dependence previously observed⁵⁻⁷ obviously stems from the use of equation (1), because from equation (4) a plot of j_R/W will always be field-dependent due to the factor $(W - W_0)/W$. This is readily demonstrated by con-

necting the measuring points of Fig. 1 with the origin [Fig. 2(a)] and plotting the slope of these straight lines (which is $\sim j_R/W$) against the average electric field at which the points have been taken [Fig. 2(b)]. For comparison we have also plotted the (normalized) values of e_p^t published by Tasch and Sah.⁵ The good agreement between these two plots [Fig. 2(b)] shows that there is obviously no discrepancy between the experimental data and that the apparent field-dependence of the thermal emission rate, e_p^t , found by these authors⁵ is caused by neglecting recombination processes at the ends of the transition region.

In conclusion we have shown that for the determination of thermal emission rates from dark leakage currents, recombination at the ends of the space charge regions has to be taken into account. Using equation (3) instead of equation (1), evidence has been given that within the experimental error the thermal emission rate of holes, e_p^t , for the Au acceptor level in silicon is field-independent for average electric fields below 10^5 V/cm. More detailed results will be published elsewhere.⁸

REFERENCES

1. WUEISSER H.J., *Festkörperprobleme XI*, Vieweg, Braunschweig (1971).
2. SAH C.T., FORBES L., ROSIER L.L. and TASCH A.F. Jr., *Solid-St. Electron.* **13**, 759 (1970).
3. TANG L.H., *J. appl. Phys.* **42**, 4101 (1971).
4. BJÖRKLUND G. and GRIMMEISS H.G., *Solid-St. Electron.* **14**, 589 (1971).
5. TASCH A.F., Jr. and SAH C.T., *Phys. Rev.* **B1**, 800 (1969).
6. YAU L.D. and SAH C.T., *Phys. Status Solidi (a)* **6**, 561 (1971).
7. ROSIER L.L. and SAH C.T., *Solid-St. Electron.* **14**, 41 (1971).
8. BRAUN S. and GRIMMEISS H.G., to be published.
9. SHOCKLEY W. and READ W.T., *Phys. Rev.* **87**, 835 (1952).
10. For PIN structures W can be considered as voltage insensitive for high reverse bias conditions and W_0 will decrease monotonically with increasing reverse bias giving a comparable voltage dependence for $(W - W_0)/W$ as in the case of a PN junction.

Die thermische Emissionsgeschwindigkeit der Löcher e_p^t wurde mit Hilfe des Dunkelsperrstromes für den Goldakzeptor in Siliziumdioden bei verschiedenen elektrischen Feldern gemessen. Die Ergebnisse zeigen, dass e_p^t für ein durchschnittliches elektrisches Feld kleiner 10^5 V/cm feldunabhängig ist.

Thermal and optical generation current in reverse-biased gold-doped silicon P⁺N junctions without the depletion approximation

by S Braun and H G Grimmeiss

Lund Institute of Technology, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

Abstract

Optical and thermal generation currents in reverse-biased P-N junctions have been calculated for an exponential tail of free charge carriers extending from the neutral regions into the transition region. Net generation of electron-hole pairs can then be neglected at the ends of the transition region because of recombination processes. The width W_0 of these regions has been calculated for step junctions and asymmetrical linearly-graded junctions. For a symmetrical step junction, W_0 is independent of bias at constant temperature and constant illumination intensity. For a linearly-graded junction, however, the widths of these regions become monotonically smaller with increasing reverse bias. In all cases, the regions with negligible net generation decrease logarithmically with intensity. The calculations are in good agreement with experimental results for gold-doped silicon diodes. Furthermore, it is shown that, for moderate average electric fields, neither the optical nor the thermal emission rates for the gold acceptors in silicon are field-dependent.

Thermal and optical generation current in reverse-biased gold-doped silicon P^+N junctions without the depletion approximation

by S Braun and H G Grimmeiss

Lund Institute of Technology, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

1. Introduction

In contrast to the shallow impurity levels used in semiconductor technology, deep-lying impurity levels are not yet adequately understood. These centres, however, very often determine minority carrier lifetime and are therefore of great importance for the physical properties of semiconducting materials. From the experimental point of view, a deep centre level is characterized by its position in the forbidden energy gap and its capture and emission rates for electrons and holes. Recently several new methods have been developed ¹⁾²⁾³⁾ to measure these quantities more accurately. Most of these techniques make use of extrinsic excitation processes in P-N junctions and the results are interpreted with the assumption that excitation rates are constant in the entire space charge region. This is a good approximation when the excitation is caused by interband transitions or transitions via shallow impurity levels. In a previous paper ⁴⁾, however, it has been shown that this approximation fails when the thermal generation in the space charge region occurs mainly via deep impurity levels because of competing recombination processes due to free carrier tails extending from the neutral regions into the space charge region. As a direct consequence it could further be shown that the previously-observed field-dependence of the product of the dark leakage current and the diode capacitance ⁵⁾ is caused by the above approximation and that it is not necessary to assume a field-dependence of the thermal emission rates ⁶⁾ in gold doped silicon. Hence, for all techniques using extrinsic excitation processes in reverse-biased PN junctions

for studying the fundamental physical properties of deep level impurities, it should be of importance to know in which part of the space charge region the net excitation rate can be neglected.

The purpose of this paper is therefore to calculate the region in different types of P-N junctions where the net thermal and optical excitation cannot be neglected and to investigate how the width of this region is influenced by reverse bias, illumination intensity and temperature. In addition, experimental results obtained with gold-doped silicon diodes will be presented and compared with calculations.

2. Theory

2.1 Background

The experiments of this paper make use of reverse-biased P^+N silicon junctions which are doped with gold impurities. Using Shockley-Read-Hall statistics ⁷⁾⁸⁾, it is readily shown that during illumination the net rate of electron emission from a single impurity level is given by

$$U_{cn} = \frac{n_1 f_t}{\tau_{no}} + g_n^o - \frac{n f_{tp}}{\tau_{no}} \quad (1)$$

and the corresponding net rate of hole emission as

$$U_{cp} = \frac{p_1 f_{tp}}{\tau_{po}} + g_p^o - \frac{p f_t}{\tau_{po}} \quad (2)$$

where $g_n^o = e_n^o N_{TT} f_t = \sigma_n^o I N_{TT} f_t$ and $g_p^o = e_p^o N_{TT} f_{tp} = \sigma_p^o I N_{TT} f_{tp}$ are the optical-generation rates of electrons and holes, respectively. Otherwise the same notations as in ref 7 have been used.

From the steady state condition $U_{cn} = U_{cp} = U$, the total net emission rate can be calculated from equ 1 and 2

$$U = \frac{e_n^o e_p^o N_{TT}^2 + e_n^o N_{TT} p_1 / \tau_{po} + e_p^o N_{TT} n_1 / \tau_{no} + (n_1 p_1 - np) / \tau_{no} \tau_{po}}{(n+n_1) / \tau_{no} + (p+p_1) / \tau_{po} + (e_n^o + e_p^o) N_{TT}} \quad (3)$$

Assuming that the quasi-Fermi levels are constant across the space charge region ⁹⁾ of a P-N junction, it is readily seen that within

the transition region of the junction we have

$$np = n_n p_p e^{-\frac{q(V_D+V_R)}{kT}} = n_l p_l e^{-\frac{qV_R}{kT}} \quad (4)$$

where V_D is the built-in voltage and V_R the reverse bias. Inserting equ 4 in equ 3 we find for the net emission rate in the transition region W of a P-N junction during illumination

$$U = \frac{e_n^0 e_p^0 N_{TT}^2 + e_n^0 N_{TT} p_l / \tau_{po} + e_p^0 N_{TT} n_l / \tau_{no} + n_l p_l (1 - e^{-\frac{qV_R}{kT}}) / \tau_{no} \tau_{po}}{(n+n_l) / \tau_{no} + (p+p_l) / \tau_{po} + (e_n^0 + e_p^0) N_{TT}} \quad (5)$$

Hence for intensities such that $(e_n^0 + e_p^0) N_{TT} \ll n / \tau_{no}, p / \tau_{po}^{10}$, the transition region W can be divided into three distinct regions depending on which term in the denominator is dominant (fig 1). The boundaries x_1 and x_2 between these regions are given by the conditions

$$n / \tau_{no} = n_l / \tau_{no} + p_l / \tau_{po} + (e_n^0 + e_p^0) N_{TT} \quad (6)$$

and

$$p / \tau_{po} = n_l / \tau_{no} + p_l / \tau_{po} + (e_n^0 + e_p^0) N_{TT} \quad (7)$$

respectively. Denoting the edges of the transition region by x_n and $-x_p$ where $W = x_n + x_p$ (fig 1), the denominator in the region $x_n - x_2$, which is close to the neutral N-region can then be approximated by n / τ_{no} . Similarly, in the region $x_1 + x_p$ close to the neutral p-region, the denominator reduces to p / τ_{po} . Because n and p increase exponentially when going from x_2 to x_n and from x_1 to $-x_p$, respectively, the net emission rate in these regions can thus be neglected with respect to that in the middle part of the transition region $W - W_0 = x_2 - x_1$ where the net emission rate is given by

$$U = \frac{e_n^0 e_p^0 N_{TT}^2 + e_n^0 N_{TT} p_l / \tau_{po} + e_p^0 N_{TT} n_l / \tau_{no} + n_l p_l (1 - e^{-\frac{qV_R}{kT}}) / \tau_{no} \tau_{po}}{n_l / \tau_{no} + p_l / \tau_{po} + (e_n^0 + e_p^0) N_{TT}} \quad (8)$$

For the purpose of discussion, we will consider the case of a deep level located in the top half of the forbidden band gap at energy E_T (i.e. $n_l \gg p_l$). In darkness, equ 8 reduces then to

$$U(\text{darkness}) = \frac{n_1^2 (1 - e^{-\frac{qV_R}{kT}})}{n_1 \tau_{po}} \quad (9)$$

in agreement with previous results ⁴⁾ if $n_1 \gg p_1 \frac{\tau_{no}}{\tau_{po}}$. It should be noted that $n = n_1$ and $p = n_1$ correspond to positions in the transition region W at which the quasi-Fermi level for electrons coincides with the deep impurity level and the distance from the quasi-Fermi level for holes to the valence band edge is $E_C - E_T$, respectively (fig 1). Hence the width W_0 of the two regions at the ends of the transition region where the net emission process can be neglected increases with increasing depth of the impurity level. Only for shallow impurity levels is W_0 small. It will, however, be shown later that for impurity levels close to the middle of the forbidden bandgap (as for instance the gold acceptor level in silicon), W_0 is larger than half the transition region for reverse bias up to about 1,5 V.

An accurate knowledge about W_0 and its voltage-dependence is therefore not only important for a calculation of the dark leakage current ⁴⁾⁶⁾¹¹⁾ and the photocurrent ¹²⁾ but also for all techniques using capacity measurements ¹⁾ because the occupancy of the deep level impurity centres can only be changed by thermal or optical excitation processes in the region $W - W_0$.

2.2 Step junctions

Rewriting equ 6 and 7 we find that, in darkness,

$$n(x_2) = n_1 \left(1 + \frac{p_1}{n_1} \frac{\tau_{no}}{\tau_{po}} \right) \quad (10)$$

$$p(x_1) = n_1 \frac{\tau_{po}}{\tau_{no}} \left(1 + \frac{p_1}{n_1} \frac{\tau_{no}}{\tau_{po}} \right) \quad (11)$$

Taking arbitrarily the electrostatic potential Φ equal to zero at $x = x_n$, it follows from equ 10 that for a step junction x_2 can be calculated from

$$\begin{aligned} \frac{qN_d}{2\epsilon\epsilon_0} (x_n - x_2)^2 &= -q\Phi(x_2) \\ &= -kT \ln\left(1 + \frac{p_1}{n_1} \frac{\tau_{no}}{\tau_{po}}\right) + (E_{Fn} - E_T)_{\text{neutral region}} \end{aligned} \quad (12)$$

where N_d is the concentration of shallow donor levels in the N region and ϵ the dielectric constant.¹³⁾ In a similar way x_1 is calculated from equ 11. Because $E_{Fn} - E_T$ will be constant in the neutral N region, $x_n - x_2$ will also be constant. This, however, means that W_0 is voltage independent if the metallurgical junction lies between x_1 and x_2 and that a plot of the dark leakage current against the width W of the transition region gives a straight line⁴⁾ with an intercept on the positive abscissa (fig 2, curve 1).

The situation is somewhat different for a one-sided step junction. In the case of a P^+N junction for example, the region $x_1 + x_p$ at the end of the space charge layer where the net emission process can be neglected, will monotonically decrease with increasing reverse bias. Only that part of W_0 , $x_n - x_2$, which is close to the lower doped side of the sample will still be voltage independent (fig 1). Hence a plot of the dark leakage current against the width W of the transition region will only asymptotically approach a straight line (fig 2, curve 2). Extrapolating this line the intercept on the positive abscissa will be equal to $x_n - x_2$, i.e. the voltage independent part of W_0 .

In many cases, however, it is difficult to produce real one-sided step junctions, although they are very useful for photocapacity measurements¹⁾. A closer inspection often shows that these "step" junctions have an exponential concentration distribution close to the metallurgical junction. In the following chapter we will therefore present more detailed calculations of the extrinsic photocurrent and dark leakage current in reversed-biased linearly-graded P^+N junctions.

2.3 Linearly graded junctions

For a charge distribution as indicated in fig 3 the potential distribution in the positive space charge region may be expressed by

$$\begin{aligned}\Phi &= - \frac{e a}{6 \epsilon \epsilon_0} (x^3 - 3x_n^2 x + 2x_n^3) = \\ &= - \frac{e a}{6 \epsilon \epsilon_0} (x_n - x)^2 [3x_n - (x_n - x)]\end{aligned}\quad (13)$$

where we have again taken as an arbitrary choice the electrostatic

potential equal to zero at $x = x_n$. a is the impurity concentration gradient.

Taking $-\Phi = V_D + V_R$ at $x = -x_p$ and assuming that Φ is continuous at $x = 0$ we find

$$V_D + V_R = \frac{e a x_n^3}{3\epsilon\epsilon_0} \left(1 + \frac{3 a x_n}{8 N_a} \right) \quad (14)$$

For a P^+N junction with $N_a \gg a x_n$ and $W \approx x_n$, equ 14 reduces to

$$V_D + V_R \approx \frac{e a W^3}{3\epsilon\epsilon_0} \quad (15)$$

Equ 13 then describes the potential distribution in the total space charge region. As in the case of a step junction, the transition region W can be divided into three distinct regions depending on which term dominates in the denominator of equ 5. The potential at the boundaries x_1 and x_2 as defined by equ 6 and 7 are then given according to equ 13 by

$$\Phi(x_1) = - \frac{e a}{6\epsilon\epsilon_0} (x_n - x_1)^2 [3 W - (x_n - x_1)] \quad (16)$$

and

$$\Phi(x_2) = - \frac{e a}{6\epsilon\epsilon_0} (x_n - x_2)^2 [3 W - (x_n - x_2)] \quad (17)$$

It is easily seen that, for a constant potential, $x_n - x_2$ and $x_n - x_1$ will never be constant for various reverse bias because of the voltage dependence of W . Consequently a plot of the reverse current against the width W of the transition region will not give a straight line (fig 2, curve 3).

Solving equ 16 and 17 we find for the position of the boundaries in the transition region

$$x_1 = W \left\{ 1 + 2 \cos \left[\frac{1}{3} \arccos \left(1 + \frac{\Phi(x_1)}{V_D + V_R} \right) + 240^\circ \right] \right\} \quad (18)$$

$$x_2 = W \left\{ 1 + 2 \cos \left[\frac{1}{3} \arccos \left(1 + \frac{\Phi(x_2)}{V_D + V_R} \right) + 240^\circ \right] \right\} \quad (19)$$

where $x_2 - x_1 = W - W_0$. Because the thermal emission rates of electrons e_n^t and holes e_p^t are equal to $n_1/\tau_{no} N_{TT}$ and $p_1/\tau_{po} N_{TT}$ respectively, the potential at $x = x_1$ and $x = x_2$ can be written as ¹³⁾

$$\Phi(x_2) = \frac{kT}{q} \ln\left(\frac{e_n^t + e_p^t + e_n^o + e_p^o}{e_n^t} \right) - \frac{1}{q} (E_{Fn} - E_T)_{\text{neutral region}}$$

and

$$\Phi(x_1) = -(V_D + V_R) + (E_T - E_{Fp})_{\text{neutral region}} - \frac{kT}{q} \ln\left(\frac{e_n^t + e_p^t + e_n^o + e_p^o}{e_p^t} \right)$$

These results clearly show that x_1 and x_2 are rather insensitive to illumination.

3. Current density in reverse-biased P-N junctions

Using equ 8 the current density for reverse-biased P^+N junctions during illumination is given by

$$J_R^{o+t} = q(x_2 - x_1) \cdot \frac{e_n^o e_p^o N_{TT}^2 + e_n^o N_{TT} p_1 / \tau_{po} + e_p^o N_{TT} n_1 / \tau_{no} + n_1 p_1 (1 - e^{-\frac{qV_R}{kT}}) / \tau_{no} \tau_{po}}{n_1 / \tau_{no} + p_1 / \tau_{po} + (e_n^o + e_p^o) N_{TT}} \quad (20)$$

Taking

$$\frac{e_p^t}{e_n^t} = \frac{p_1 \tau_{no}}{n_1 \tau_{po}} = A, \quad (21)$$

$$\frac{e_n^o}{e_n^t} = B \quad (22)$$

and

$$\frac{e_p^o}{e_n^o} = S, \quad (23)$$

equ 20 may be rewritten as

$$J_R^{o+t} = q(x_2 - x_1) e_n^t N_{TT} \frac{(A + S + BS) B + A (1 - e^{-\frac{qV_R}{kT}})}{A + B + BS + 1} \quad (24)$$

where $V_R = \frac{qa}{3\epsilon\epsilon_0} \{W^3(V_R) - W^3(0)\}$ for linearly-graded junctions and $V_R = \frac{qN_d}{2\epsilon\epsilon_0} \{W^2(V_R) - W^2(0)\}$ for one-sided step junctions.

A is a function of the temperature whereas S depends on the energy $h\nu$ of the photons used for illumination¹²⁾. It follows from equ 22 that B in contrast to S depends on intensity. As will be shown in the next chapter, B can easily be measured experimentally. As already mentioned, $x_2 - x_1$ depends on the type of junction and has to be calculated from equ 10 and 11 for a step junction and from equ 18 and 19 for a linearly-graded junction.

In darkness (i.e. $B = 0$), equ 24 reduces to

$$J_R^t = q(x_2 - x_1) \frac{e_n^t e_p^t}{e_n^t + e_p^t} N_{TT} \left(1 - e^{-\frac{qV_R}{kT}}\right) \quad (25)$$

In silicon the gold impurity has an acceptor level at about 0.55 eV below the conduction band edge and a donor level at about 0.35 eV above the valence band edge. The thermal excitation occurs therefore almost completely via the gold acceptor level. Thus taking $E_C - E_T = 0.55$ eV and $N_d = N_a = 5 \cdot 10^{15} \text{ cm}^{-3}$, $x_2 - x_1$ can be determined from equ 10 and 11 for a symmetrical step junction and the dark leakage current density J_R^t as a function of W can be calculated using Tasch and Sah's values for A⁶⁾ (fig 2). In a similar way, J_R^t can also be calculated for a one-sided step P^+N junction taking $N_a \gg N_d = 5 \cdot 10^{15} \text{ cm}^{-3}$ (fig 2).

For comparison we have also plotted the dark leakage current J_R^t against W for a linearly-graded P^+N junction. $x_2 - x_1$ has been determined in this case from equ 18 and 19, where for example $\Phi(x_1) = -1.023$ V and $\Phi(x_2) = -0.418$ V if $V_R = 0.552$ V. It is clearly seen (fig 2) that no straight line is obtained for a linearly-graded junction because of the voltage dependence of W_0 . To demonstrate how sensitive to voltage W_0 is, x_1 and x_2 have been plotted as a function of the reverse bias V_R together with the width W of the total transition region using equ 18 and 19 (fig 4). For a reverse bias $V_R = 10$ V, it is readily seen that W_0 should comprise 20 % of the total transition region. The situation is much worse for $V_R = 1$ V where W_0/W should be 0.58. For comparison, x_1 and x_2 have also been plotted for $B \neq 0$. As expected from equ 19 and 20, the increase of $x_2 - x_1$ due to illumination ($B = 7.33$) is only small.

4. Experimental results

The voltage dependence of $(W-W_0)/W$ and thus the influence of recombination processes at the ends of the transition region on the dark leakage current has been discussed previously ⁴⁾ for one-sided step junctions in gold doped silicon. In what follows we have therefore restricted all measurements to linearly-graded P⁺N silicon junctions doped with gold.

All current measurements have been performed with a Keithley electrometer 640 in conjunction with a Mosley strip card recorder 7101 BM. As light sources, an incandescent lamp with a Zeiss MM12 prism double monochromator or a ^(0.75 m)Jarrel-Ash double Czerny-Turner scanning spectrometer were used. For capacitance measurements, a Boonton capacitance bridge type 75 D was employed and voltages were measured with a HP digital voltmeter type 3450 A.

Plotting the diode capacitance C in darkness as C^{-3} against reverse bias V_R , a straight line was obtained for all diodes. Extrapolating the straight line (fig 5) an intercept on the abscissa at $V_R = -1$ V was observed and from the slope a concentration gradient $a = 1.7 \cdot 10^{19} \text{ cm}^{-4}$ was calculated. Furthermore from this curve the width W of the total transition region is easily calculated as a function of reverse bias (fig 5). Hence, measuring the voltage dependence of the dark leakage current J_R^t and plotting J_R^t against W , curve 1 in fig 6 was obtained. For comparison we have replotted the calculated curve of a linearly-graded P⁺N junction from fig 2 (solid curve 1 in fig 6) using the above mentioned values of A , W , a and $E_C - E_T$ for the determination of $E_C - E_{Fn} = kT \ln N_C/aW$, $\Phi(x_1)$ and $\Phi(x_2)$. The agreement at least for voltages up to 3 V is very good.

In order to investigate how x_1 and x_2 are influenced by optical excitation processes, the diodes were illuminated with photons of energy 0.885 eV and the measured photocurrent J_R^{o+t} plotted against W for different intensities. Photons of this energy mainly cause electron-hole pair generation via the gold acceptor level ¹²⁾. To compare these results with each other, the curves have been normalized by dividing the photocurrent by the net emission rate (curve 2, 3 and 4 of fig 6).

The optical excitation density has been determined experimentally by measuring the reverse current with illumination and in darkness for a constant reverse bias $V_R \gg \frac{kT}{q}$. The ratio H of these two values is obtained by dividing equ 24 with equ 25:

$$H = \frac{J_R^{o+t}}{J_R^t} = \frac{(A + AB + BS + B^2S)(1 + A)}{(1 + A + B + BS)A} \cdot \frac{(x_2 - x_1)^{o+t}}{(x_2 - x_1)^t} \quad (26)$$

According to fig 4, the last factor on the right hand side of equ 26 is very close to 1 for large reverse bias. Hence, B can be determined from the above relation by inserting A ⁶⁾ and the measured value for H . The B -values found for curve 1, 2, 3 and 4 (in fig 6) were 0, 0.192, 1.62 and 7.33. S has been determined to about 4 ¹²⁾ for photon energies $h\nu = 0.885$ eV. Thus, knowing A , B and S and determining x_1 and x_2 from equ 18 and 19, the photocurrent J_R^{o+t} as a function of the width W of the total transition region is calculated from equ 24 (fig 6, solid curves 2, 3 and 4) and can be compared with the experimentally found values.

The good agreement between the experimental and theoretical results clearly shows that the reverse current is indeed limited by recombination processes at the ends of the transition region. The decrease of the reverse current due to these recombination processes is quite substantial at small reverse bias which is readily seen by comparing the experimental results with the calculated photocurrent obtained without any recombination in the transition region (fig 6, dotted line). This in turn means that J_R is not proportional to W but to $W - W_0$ and hence the observed field dependence of J_R^t/W ⁵⁾ might not be caused by a field-dependence of the thermal emission rate at low electric fields ⁶⁾ but can be explained by the field dependence of $(W - W_0)/W$ ⁴⁾. The shift of the curves to higher currents with increasing intensity (fig 6) is due to the increase of $W - W_0 = x_2 - x_1$. In agreement with equ 18 and 19 however, the change is only small because of the small value for B obtained at 208 °K with the highest available intensity $I_{\max}$. Keeping the intensity $I_{\max}$ constant, B is substantially increased by lowering the temperature to 90 °K which at the same time causes an increase of $W - W_0$ and hence of the photocurrent (fig 6, curve 5).

The above results therefore not only explain the field dependence of the reverse current but also the temperature dependence of the photocurrent (short circuit current). Measuring the photocurrent $J_R^{o+t} - J_R^t$ in gold-doped silicon diodes at a photon energy of 0.885 eV as a function of temperature for different constant reverse bias, a pronounced temperature dependence is observed (fig 7). This temperature dependence, however, is not caused by a temperature dependence of the optical emission rates but can easily be explained with constant emission rates by making use of the above considerations. Because the gold acceptor level is located in the top half of the forbidden bandgap in silicon, e_n^t is much larger than e_p^t (6) and most of the gold acceptor levels will be empty at higher temperatures. Hence, the rate limiting process for the photocurrent is the photo excitation of electrons from the valence band into the acceptor level. With decreasing temperature, however, the thermal excitation decreases and so does the photocurrent because the hole occupancy of the gold acceptor level will change smoothly from about 1 to $e_n^o/(e_n^o+e_p^o) \approx 0,2$ (e_p^o is about 4 e_n^o for $h\nu = 0.885$ eV (12)). At these temperatures the thermal excitation processes can be neglected. According to equ 18 and 19, a further decrease of the temperature will increase $W-W_0$ and hence the photocurrent. The increase of $W-W_0$, however, is only small for larger reverse bias (fig 6). This is the reason why in this region the temperature dependence of the photocurrent is much smaller for large reverse bias than for $V_R = 0$.

5. Conclusion

The reverse current of step and linearly-graded P-N junctions has been calculated by taking into account recombination processes at the ends of the transition region. The results show that even for large reverse bias not all the transition region contributes to the thermally and optically generated reverse current. Furthermore, the part of the transition region where the reverse current is generated is increased by extrinsic illumination, although the increase is small for large reverse bias. These effects have to be considered when the fundamental physical properties of deep level impurities are measured by techniques which make use of

excitation processes via deep impurities in reverse biased P-N junctions ¹⁾. In particular it has been shown that the field-dependence of the dark leakage current can be explained by the field-dependence of $(W-W_0)/W$ and that in contrast to previous interpretations ⁶⁾ the thermal emission rate of the gold acceptor level in silicon can be considered as field-independent at low average electric fields.

6. Acknowledgement

The authors would like to thank the Swedish Natural Science Research Council who supplied the 0.75 m Jarrel-Ash double Czerny-Turner scanning spectrometer and the Swedish Council for Technical Research for their financial support.

References

1. C T Sah, L Forbes, L L Rosier and A F Tasch, Jr,
Sol-State Electron 13, 759 (1970)
2. L H Tang, J Appl Phys 42, 4101 (1971)
3. G Björklund and H G Grimmeiss, Sol-State Electron 14, 589 (1971)
4. S Braun and H G Grimmeiss, Sol State Commun 11, 1457 (1972)
5. M S Tyagi, Sol-State Electron 11, 99 (1968)
6. A F Tasch, Jr, and C T Sah, Phys Rev B 1, 800 (1970)
7. W Shockley and W T Read, Jr, Phys Rev 87, 835 (1952)
8. R N Hall, Phys Rev 86, 600 (1952)
9. A S Grove, Physics and Technology of Semiconductor Devices,
J Wiley & Sons, 1967
10. This condition is easily fulfilled in gold doped silicon if
the intensity is less than $10^{20} \text{ cm}^{-2} \text{ sec}^{-1}$.
11. P U Calzolari and S Graffi, Sol-State Electron 15, 1003 (1972)
12. S Braun and H G Grimmeiss, unpublished
13. This is readily obtained from equ 6 and the expression for
the free electron concentration at x_2 :
$$n(x_2) = N_C \exp\{[q\Phi(x_2) + E_{Fn} - E_C]/kT\} =$$
$$= n_1 \exp\{[q\Phi(x_2) + E_{Fn} - E_T]/kT\}.$$

Figures

- Fig 1 Band diagram of a P-N junction (see text).
- Fig 2 Calculated dark leakage current density J_R^t as a function of the total transition region W at 208 °K for a symmetrical step junction (curve 1), one-sided step junction (curve 2) and "one-sided" linearly-graded junction (curve 3).
- Fig 3 Schematic illustration of the charge distribution within a "one-sided" linearly-graded junction.
- Fig 4 Boundaries x_1 and x_2 within the transition region (see text and fig 1) as a function of the reverse bias V_R in darkness (x_1 ooo, x_2 $\Delta\Delta\Delta$) and during illumination (x_1 $\bullet\bullet\bullet$, x_2 $\blacktriangle\blacktriangle\blacktriangle$). For comparison the width W of the total transition region is also plotted ($\times\times\times$).
- Fig 5 C^{-3} plotted against the reverse bias V_R .
- Fig 6 Normalized reverse current against the width W of the total transition region in gold doped silicon at 208 °K in darkness (ooo) and with increasing extrinsic illumination intensity ($B = 0.192$ $\Delta\Delta\Delta$, $B = 1.62$ $\bullet\bullet\bullet$, $B = 7.33$ $+++$). For comparison the normalized reverse current at 90°K ($B = 2.3 \cdot 10^{18}$ $\square\square\square$) with the same intensity as curve 4 is also plotted. All solid lines are calculated from theory. The dotted line corresponds to the calculated photocurrent obtained without any recombination within the transition region.
- Fig 7 Photocurrent $J_R^{o+t} - J_R^t$ against temperature without and with 10 V reverse bias.

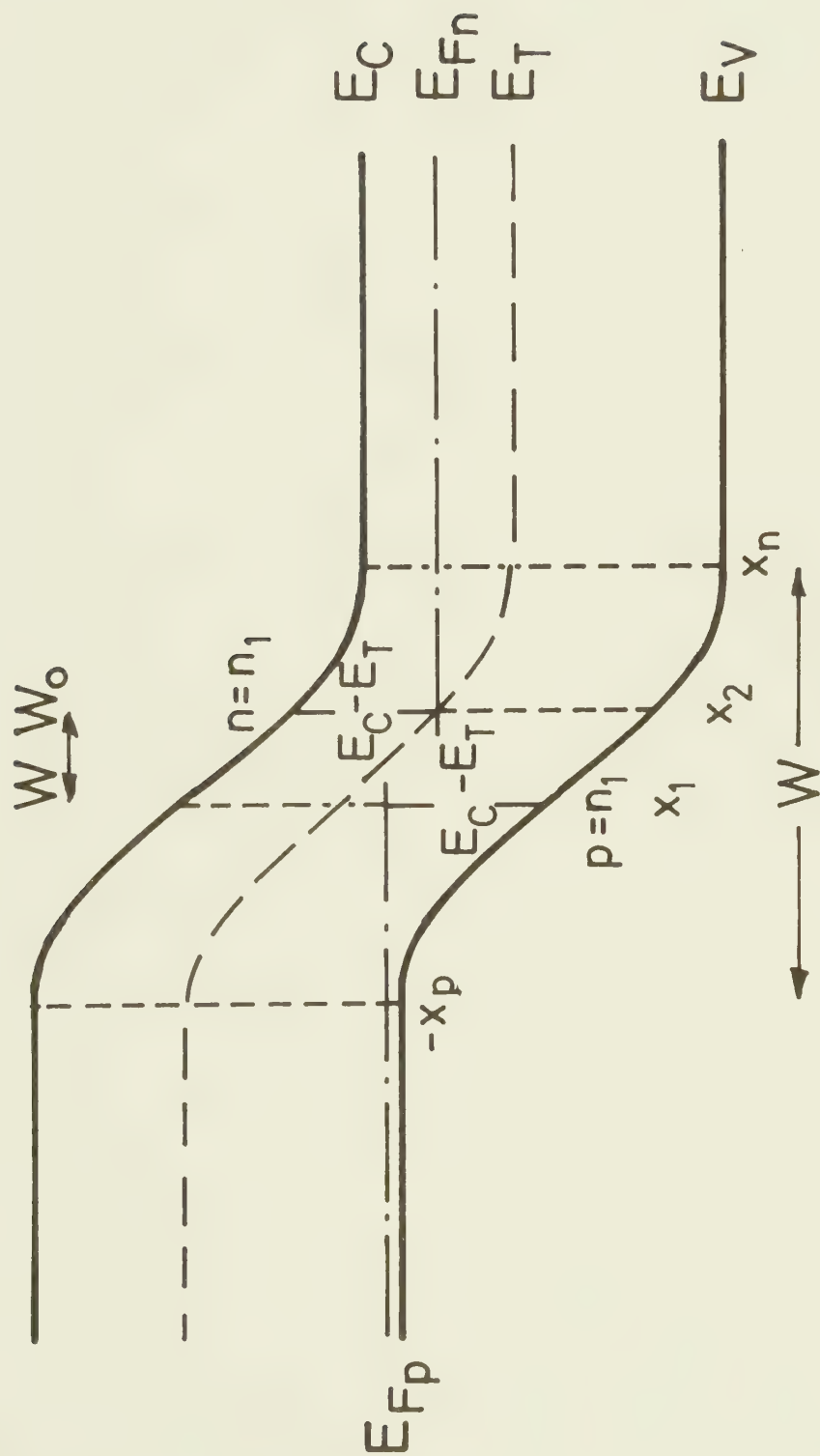


Fig 1

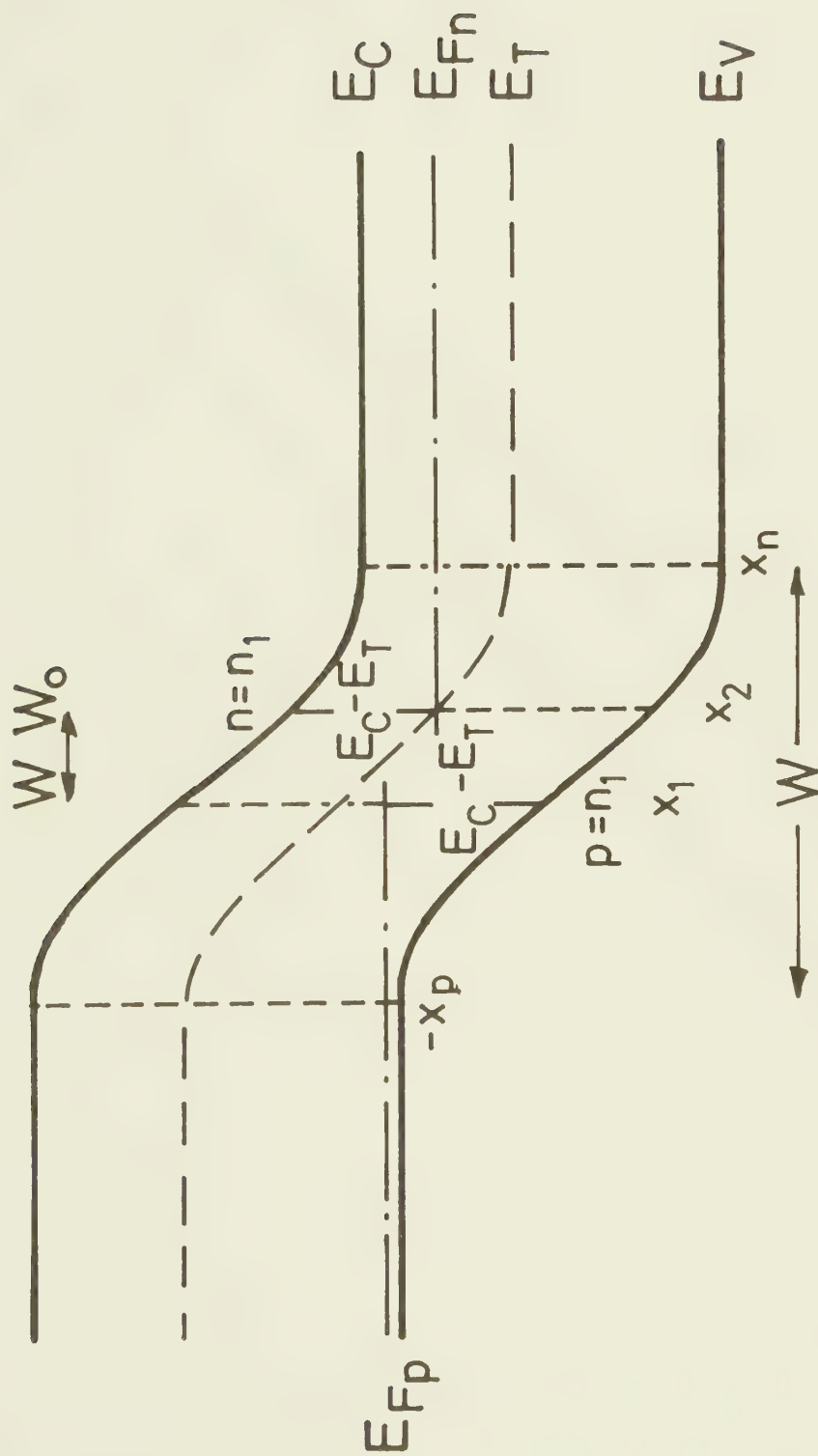


Fig 1



Fig 2

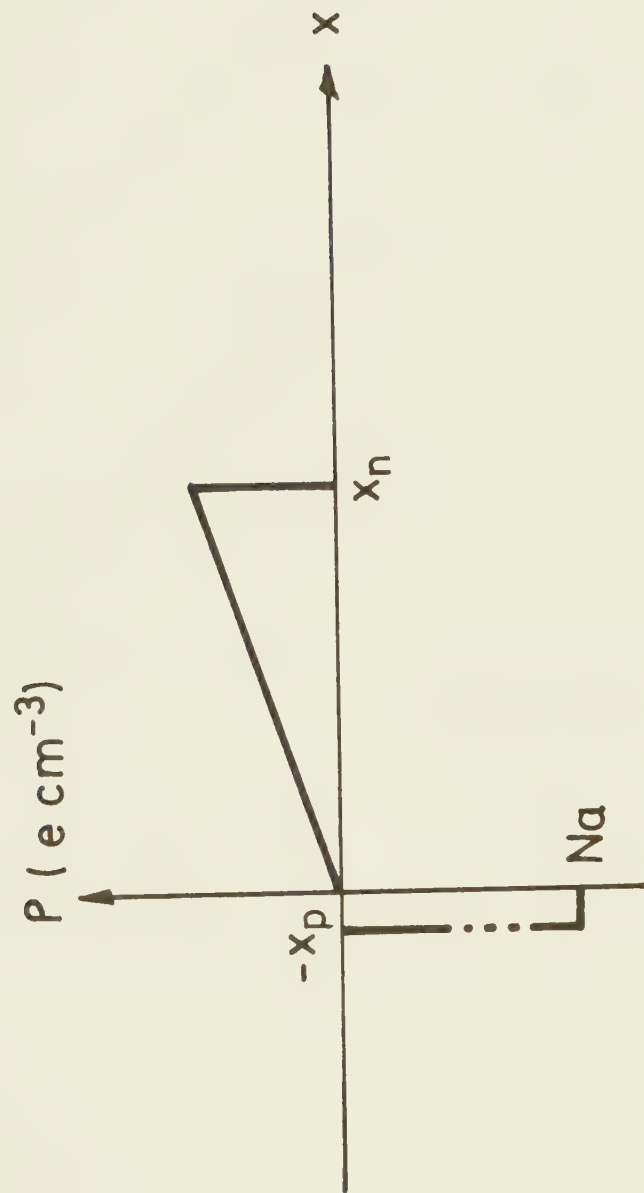


Fig 3

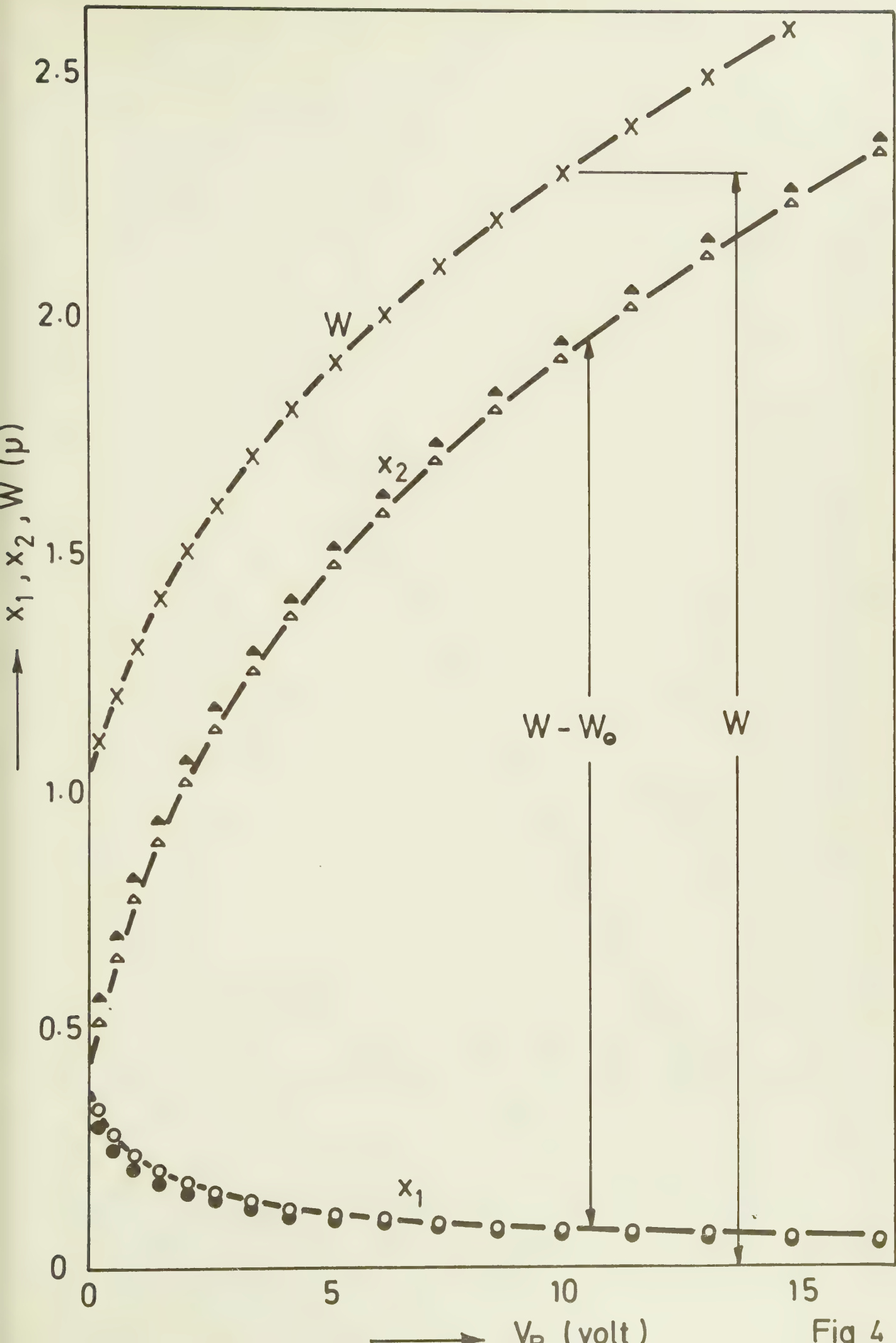


Fig 4

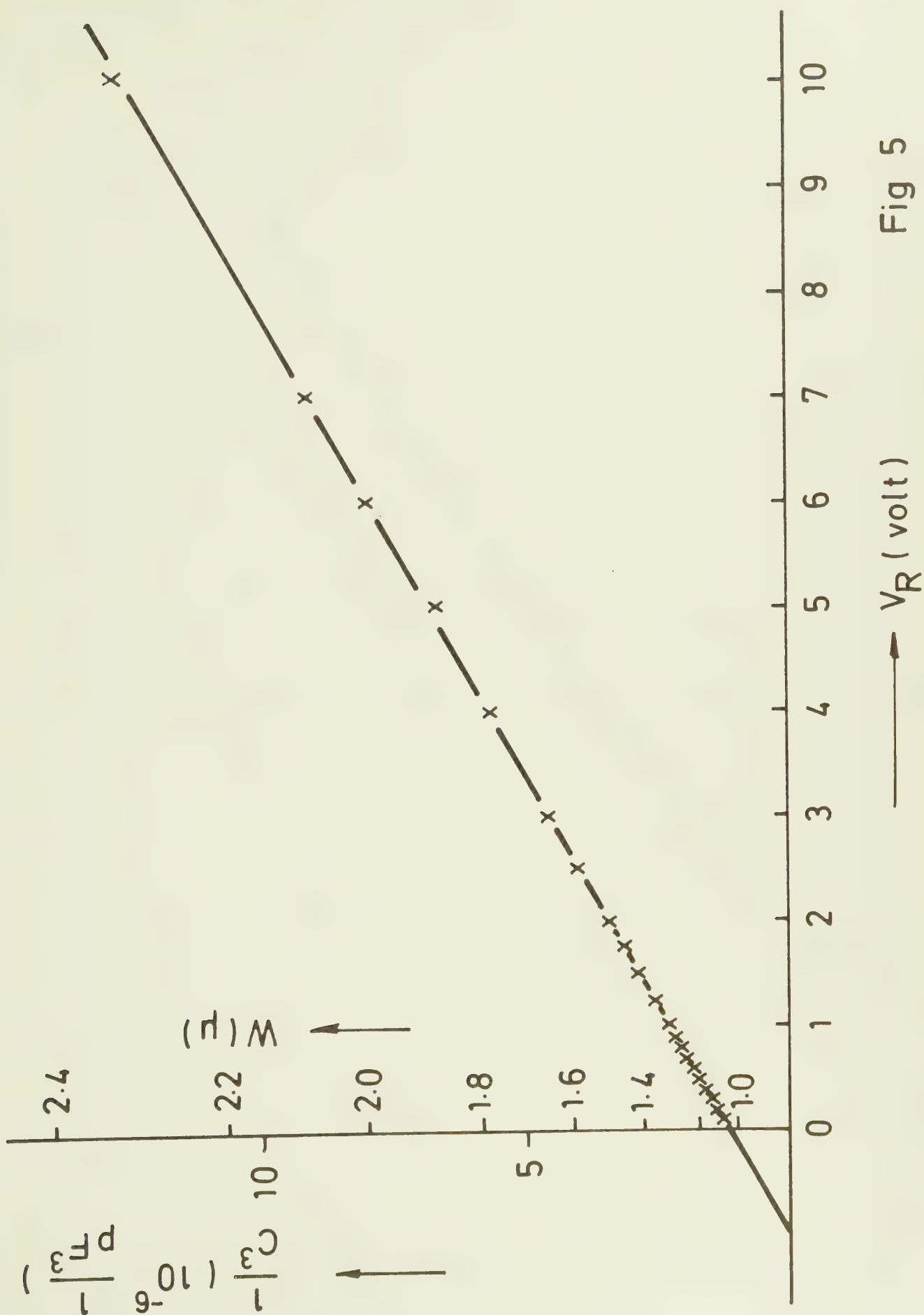


Fig 5

J_p (arb. units)

15

10

5

0

0.9

1.1

1.3

1.5

1.7

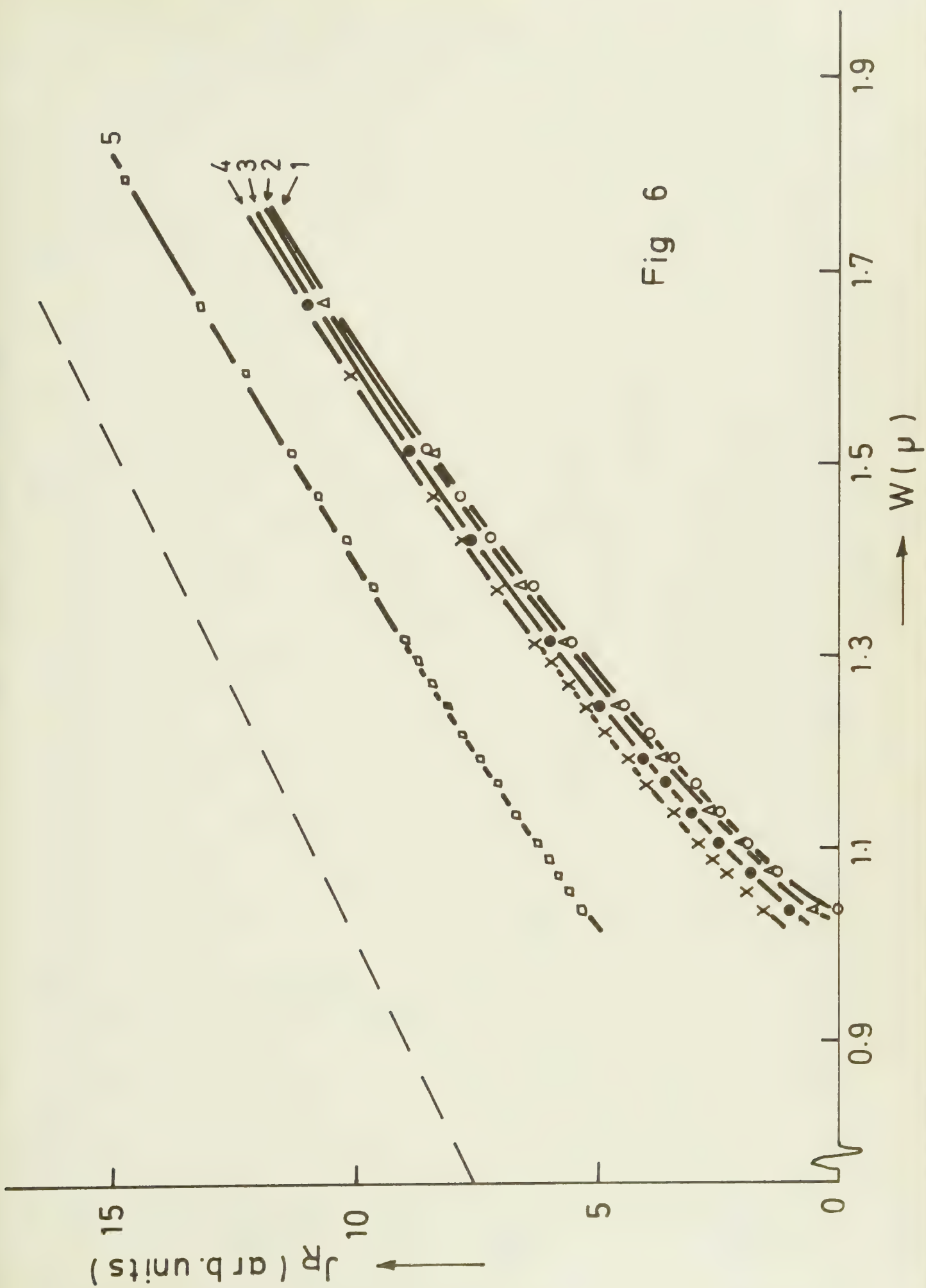
1.9

$\longrightarrow W(\mu)$

Fig 6

4
3
2
1

5



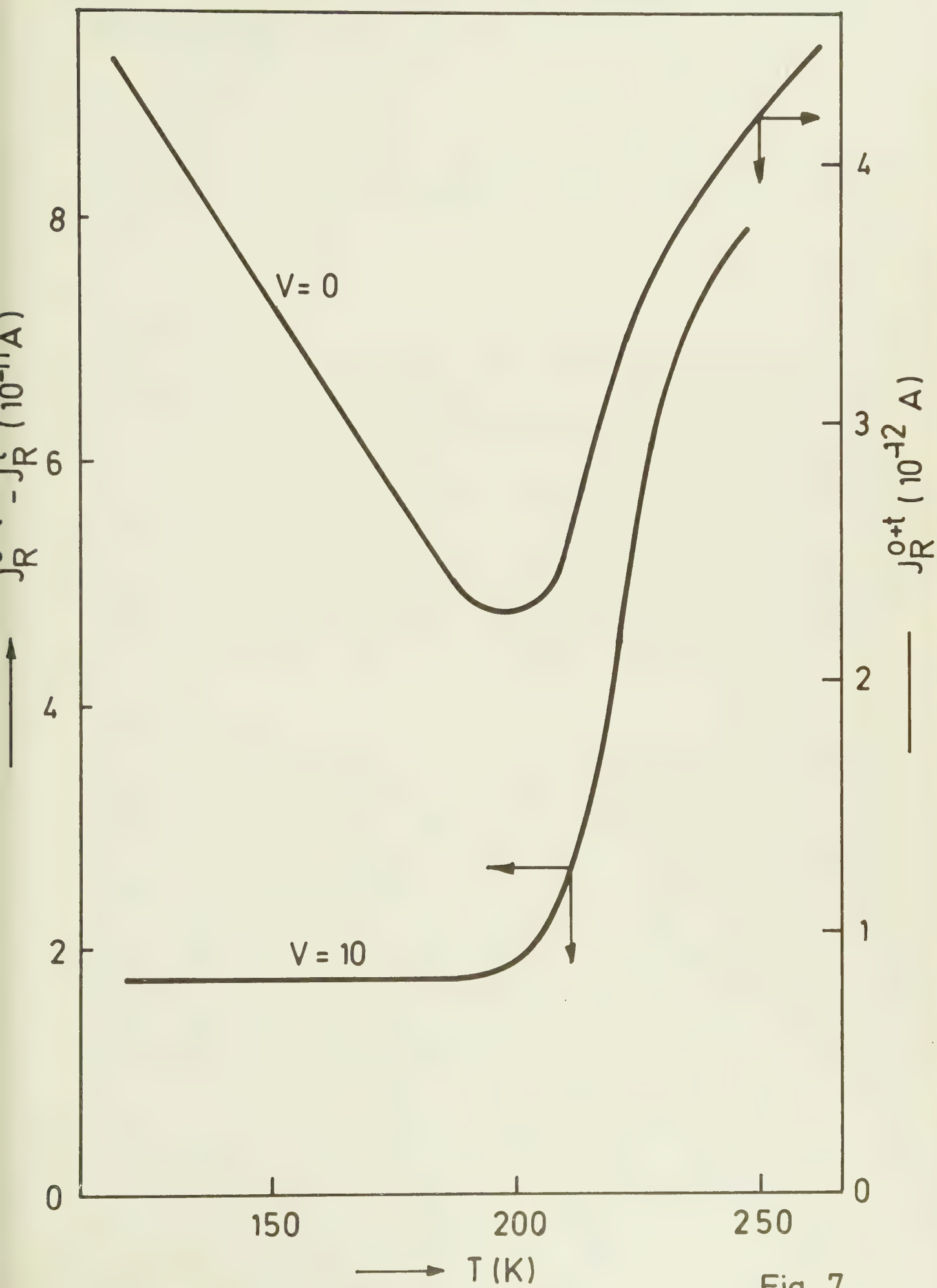


Fig. 7

Photoionization of electrons and holes at oxygen donors in gallium phosphide

by

S Braun and H G Grimmeiss

Lund Institute of Technology, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

Abstract

The spectral dependence of the photo-ionization cross-section for the oxygen donor in GaP is studied in the temperature range between 90 °K and 410 °K by steady state photocurrent measurements using two different radiation sources. From a fit of Lucovsky's model to the experimental results, accurate information is obtained about the energy position of the oxygen donor at all temperatures. It is found that the oxygen level is pinned to the valence band for temperatures above 295 °K and that at these temperatures the Franck-Condon shift is very small. This may indicate that there is little interaction between the impurity level and the surrounding lattice.

Zusammenfassung

Die spektrale Verteilung der photojonisationsquerschnitte für den Sauerstoff-Donor in GaP wurde im Temperaturbereich zwischen 90 °K und 410 °K mit Hilfe von stationären Photoströmen unter Anwendung von zwei Lichtquellen untersucht. Durch Anpassung von Lucovsky's Modell an die experimentellen Ergebnisse lässt sich die energetische Lage des Sauerstoff-Donors für alle Temperaturen genau bestimmen. Man findet, dass der energetische Abstand des Sauerstoff-Störstelle vom Valenzband für Temperaturen über 295 °K konstant und der Franck-Condon Effekt sehr klein ist. Die Wechselwirkung zwischen der Störstelle und dem Gitter ist daher vermutlich nur sehr klein.

Photoionization of electrons and holes at oxygen donors in gallium phosphide

By

S Braun and H G Grimmeiss

Lund Institute of Technology, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

In a previous paper ¹⁾ it has been shown that the extrinsic photo-current density of a reverse biased P-N junction due to the illumination with photons of energy $h\nu$ and intensity I is given by

$$J_R^{o+t} = q(W-W_0) U \quad (1)$$

where U is the total net emission rate from a single impurity level of concentration N_{TT} and $W-W_0$ is the middle part of the transition region where the photocurrent is generated. From Shockley-Read-Hall statistics ²⁾³⁾ U is readily calculated ¹⁾ as

$$U = \frac{e_n^o e_p^o N_{TT}^2 + e_n^o N_{TT} p_1/\tau_{po} + e_p^o N_{TT} n_1/\tau_{no} + n_1 p_1 (1 - e^{-\frac{qV_R}{kT}})/\tau_{no}\tau_{po}}{n_1/\tau_{no} + p_1/\tau_{po} + (e_n^o + e_p^o) N_{TT}} \quad (2)$$

where $e_n^o = \sigma_n^o I$ and $e_p^o = \sigma_p^o I$ are the optical emission rates of electrons and holes, respectively. Otherwise the same notations as in ref 2 have been used.

Hence, for $n_1/\tau_{no} N_{TT} \ll e_p^o$ and $p_1/\tau_{po} N_{TT} \ll e_n^o$ i.e. at low temperatures when thermal emission processes are negligible compared with optical excitation processes, equ 1 can be rewritten as

$$J_R^o = q(W-W_0) N_{TT} \frac{e_n^o e_p^o}{e_n^o + e_p^o} \quad (3)$$

If the junction is simultaneously illuminated with monochromatic

light of an intensity $h\nu_s < E_T - E_V$ and intensity I_s such that $e_{ns}^o \gg e_n^o + e_p^o$, the total photocurrent density calculated from equ 3 is given by ⁴⁾

$$J_{Rh}^o = q(W - W_o) N_{TT} e_p^o = c_1 e_p^o \quad (4)$$

where c_1 can be considered as constant for large reverse bias because $W - W_o$ depends only very weakly on the optical emission rates ¹⁾. Here we have assumed a deep impurity level located in the top half of the forbidden bandgap at energy E_T . The steady state photocurrent J_{Rh}^o is thus directly proportional to e_p^o . It is therefore especially suitable for the determination of threshold energies in contrast to differential methods such as measurements of photo capacitance. If, on the other hand, the intensity ratio is chosen such that $e_n^o + e_p^o \gg e_{ns}^o$, it has previously been shown ⁴⁾ that the increase in the photocurrent density ΔJ_{Rl}^o can be written as

$$\begin{aligned} \Delta J_{Rl}^o &= q(W - W_o) N_{TT} \left[\frac{e_p^o}{e_n^o + e_p^o} \right]^2 e_{ns}^o \\ &= c_2 e_{ns}^o \end{aligned} \quad (5)$$

where c_2 again is constant for large reverse bias and constant photon energy $h\nu$ of the primary light. Hence, by measuring J_{Rh}^o and ΔJ_{Rl}^o as a function of photon energy, the spectral dependence of the photo-ionization cross-sections σ_n^o and σ_p^o is obtained when in the presence of competing absorption processes. No transient measurements are involved as for photo capacitance measurements. In addition, the steady-state photocurrents J_{Rh}^o and ΔJ_{Rl}^o are independent of the type of junction and equ 4 and 5 are valid for both linearly-graded junctions and step junctions.

By combining experimental results with theoretical considerations on photo-ionization cross-sections ⁵⁾⁶⁾, accurate information is obtained about the position of deep level impurity centres. Furthermore because photocurrents are easily measured at different temperatures the temperature dependence of binding energies and thus the variation of the impurity level with respect to the bands is readily obtained. Information like these might be helpful in answering still open questions as for instance how sharply localized

wavefunctions of deep impurity levels are and how significant a strong electron-phonon coupling may be.

In this paper we report on the use of steady-state photocurrent to study GaP doped with oxygen. Substitutional oxygen causes in GaP a donor level which according to Kukimoto et al ⁷⁾ may involve two bound states. The ionization energy of the first electron has been measured by donor-acceptor-pair spectra and a value of 0.895 eV has been quoted at 1.6 °K ⁸⁾. The corresponding photo-ionization cross-sections were previously determined by Björklund and Grimmeiss ⁴⁾ at room temperature and by Kukimoto et al ⁷⁾ at 167 °K. Good agreement was found for σ_p^O whereas the data for σ_n^O were substantially different.

The spectral distribution of the relative photo-ionization cross-sections for electrons and holes obtained from steady-state photocurrents according to equ 4 and 5 are shown in fig 1 and 2 for the oxygen donor in GaP at different temperatures. An exponential tail is observed at small photon energies. For larger photon energies, however, a good agreement is obtained at all temperatures with Lucovsky's model ⁶⁾ (solid curves) by a proper choice of the threshold energy (or corresponding energy difference) as the only fitting parameter. Because this model renormalizes a delta-function potential this may indicate that the oxygen donor in GaP can be described by sharply localized wave functions. We might then expect that there is little interaction with the surrounding lattice and that relaxation effects are small.

The energy $E_C - E_T$ of the oxygen donor and the energy difference $E_T - E_V$ between the donor level and the valence band obtained by fitting Lucovsky's model to our experimental results are given in tab 1 for different temperature together with values E_g for the bandgap in GaP ⁹⁾ and the difference ΔE_g between the experimentally found $E_C - E_V$ values and E_g . Plotting $E_C - E_T$, $E_T - E_V$ and E_g as a function of temperature (fig 3), it is clearly seen that within the experimental error $E_C - E_T$ has about the same temperature dependence as E_g for all temperatures. On the other hand $E_T - E_V$ follows the bandgap only for temperatures below 270 °K and is

nearly constant at higher temperatures. This is in agreement with previous works on the temperature dependence of the photoluminescence investigated by R N Bhargava¹⁰⁾ for temperatures above 295 °K which indicate that the oxygen donor level varies little with respect to the valence band. From results obtained by using calculated emission line shapes to subtract the phonon replicas from photoluminescence spectra at 87 °K, Dishman concluded¹¹⁾ that the oxygen level is already pinned to the valence band over the range $4 \leq T \leq 87$ °K.

From tab 1, it can also be seen that ΔE_g becomes very small at elevated temperatures implying that the sum of $E_C - E_T$ and $E_T - E_V$ is very close to the bandgap in this range. Certainly, this result suggests that at these temperatures the Franck-Condon shift is small, in contrast to previous work¹²⁾ on luminescence. We conclude this letter by noting that the amount of the energy shift $E_T - E_V$ apparently depends on the Zn-O complex concentration.

The authors would like to thank the Swedish Natural Science Research Council for financial support.

References

- 1) S Braun and H G Grimmeiss, to be published in J Appl Phys
- 2) W Shockley and W T Read, Jr, Phys Rev 87, 835 (1952)
- 3) R N Hall, Phys Rev 86, 600 (1952)
- 4) G Björklund and H G Grimmeiss, Sol-State Electron 14, 589 (1971)
- 5) H B Bebb, Bull Am Phys Soc 12, 342 (1967)
- 6) G Lucovsky, Sol State Commun 3, 299 (1965)
- 7) H Kukimoto, C H Henry and G L Miller, Appl Phys Lett 21,
251 (1972)
- 8) P J Dean, C H Henry and C J Frosch, Phys Rev 168, 812 (1968)
- 9) M B Panish and H C Casey, Jr, J Appl Phys 40, 163 (1969)
- 10) R N Bhargava, J Appl Phys 41, 3698 (1970)
- 11) J M Dishman, Phys Rev B 3, 2588 (1971)
- 12) T N Morgan, M H Pilkuhn and M R Lorenz, IBM Research Paper
RC-1612 (1966)

Figures

- 1) Spectral dependence of the logarithm of the photo-ionization cross-section σ_n^0 for the excitation of electrons from the oxygen donor level into the conduction band in GaP:Zn,O at 90 °K (xxx), 195 °K (ooo), 295 °K (vvv), 340 °K (●●●) and 410 °K (△△△). The solid curves are calculated from Lucovsky's model ⁶⁾.
- 2) Spectral dependence of the logarithm of the photo-ionization cross-section σ_p^0 for the excitation of electrons from the valence band into the oxygen donor level in GaP:Zn,O at 90 °K (xxx), 195 °K (ooo) and 295 °K (●●●). For temperatures above 295 °K similar results as for 295 °K have been obtained. The solid curves are calculated from Lucovsky's model ⁶⁾.
- 3) Plot of $E_C - E_T$ (●●●), $E_T - E_V$ (ooo) and E_g (—) against temperature (see text).

TABLE. 1

$T^{\circ}K$ \ eV	$E_c - E_T$	$E_T - E_v$	$(E_c - E_T) + (E_T - E_v)$	E_g	ΔE_g
90	0.945	1.470	2.415	2.329	0.086
195	0.910	1.440	2.355	2.302	0.053
295	0.870	1.400	2.270	2.267	0.003
340	0.845	1.400	2.245	2.248	- 0.003
380	0.840	1.395	2.240	2.231	0.009
410	0.825	1.395	2.220	2.218	0.002

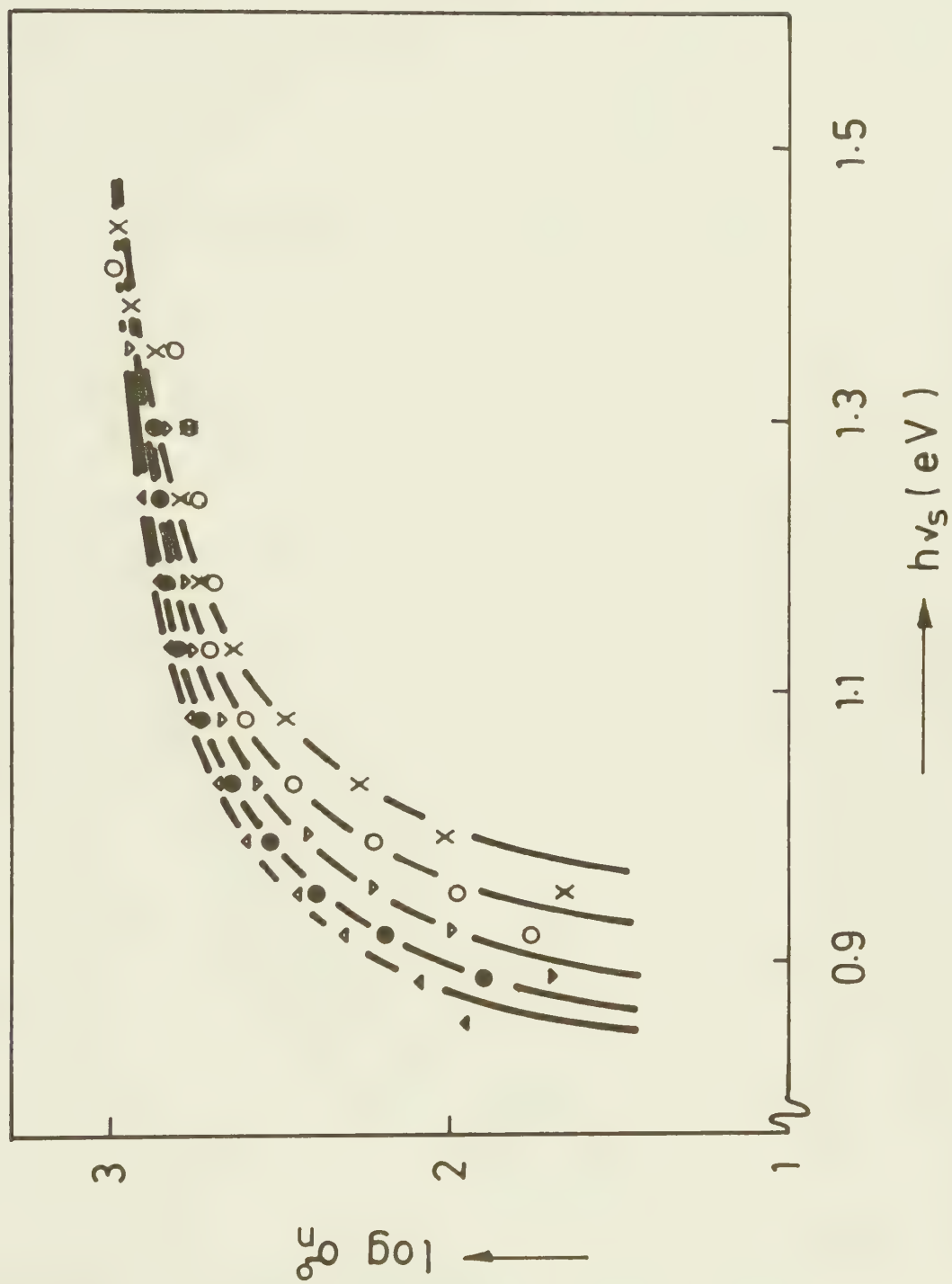


Fig 1



Fig 2

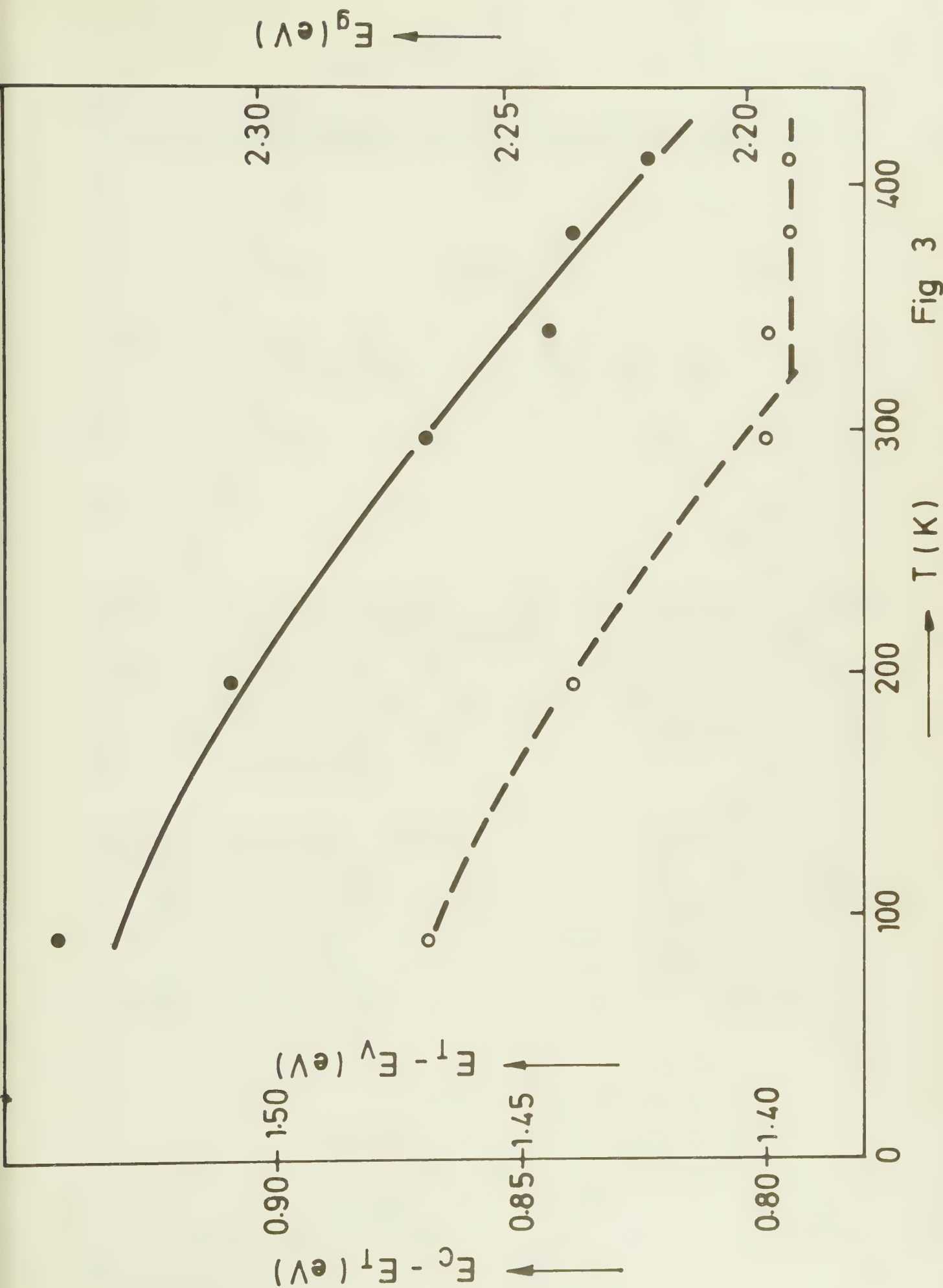


Fig 3

PHOTOCAPACITANCE MEASUREMENTS OF THE ENERGY LEVELS IN ZnSe:Mn

S BRAUN (a) H G GRIMMEISS (a) J W ALLEN (b)

Department of Solid State Physics, Lund Institute of Technology
S-220 07 Lund 7, Sweden (a) and

Department of Physics, University of St Andrews, Fife, Scotland (b)

Photocapacitance measurements, using two simultaneous sources of illumination, show that manganese introduces an energy level in ZnSe which is 2.0 eV below the conduction band and 0.65 eV above the valence band at room temperature. There is some evidence that when the level is filled the manganese is in the d^5 configuration.

Unter gleichzeitiger Verwendung von zwei Lichtquellen wird mit Hilfe von Photokapazitätsmessungen gezeigt, dass Mangan in ZnSe ein Energieniveau hervorruft, das bei Zimmertemperatur 2.0 eV unterhalb des Leitungsbandes und 0.65 eV oberhalb des Valenzbandes liegt. Es besteht Grund zur Annahme, dass das Mangan sich in der d^5 Konfiguration befindet, wenn das Niveau besetzt ist.

Department of Solid State Physics, Lund Institute of Technology, S-220 07 Lund 7, Sweden (a) and Department of Physics, University of St Andrews, Fife, Scotland (b)

PHOTOCAPACITANCE MEASUREMENTS OF THE ENERGY LEVELS IN ZnSe:Mn

S BRAUN (a) H G GRIMMEISS (a) J W ALLEN (b)

1. INTRODUCTION

Measurements of photoconductivity can give a great deal of information concerning the properties of impurities in semiconductors. If the semiconductor is highly conducting then the method is often not applicable because the photosignal may be much less than the current noise. One way of overcoming this limitation is to remove free carriers from some region of the material by forming a rectifying junction, for then the photoresponse of the junction may be greater than the junction dark current. For example, Grimmeiss and Olofsson [1] investigated the properties of GaP:Cu in this way using an alloyed diode and Björklund and Grimmeiss [2] investigated the oxygen level in epitaxial GaP junctions. One may measure the effect of light on either the charge in the junction or the rate of flow of charge across the junction. The former is a photocapacitance measurement, the latter a photocurrent, or equivalently

a photovoltage, measurement. Variations of these methods can give information on photoionization cross-section spectra [2,3], impurity concentration [2,4], thermal emission rates [5] and so on. In general, photocurrent or photovoltage measurements give more accurate data because one is usually measuring a large signal on a small background whereas in the photocapacitance methods one measures a small change on a large background. Photocapacitance measurements, however, can give valuable information on the sign of photo-induced charge changes.

If one wants information on impurities in bulk material, there is an advantage in using Schottky barrier diodes since the depletion region is then of the same composition as the bulk material, unaffected by alloying or diffusion. However, in this case an extra complication arises in measuring photocurrent or photovoltage if one works in a spectral region where photoemission from the metal to the semiconductor gives an important contribution to the current. We have shown, in work to be reported elsewhere, that this effect can be separated from the impurity effect by using time discrimination. Photocapacitance measurements are not seriously affected by photoemission.

The material investigated here is ZnSe:Mn. Although transition metal impurities are of considerable importance as radiative or non-radiative recombination centres in semiconductors and phosphors, there is no adequate theory of their energy levels with respect to the host crystal energy levels. Experimental evidence is therefore valuable in throwing light on the problem. In addition, ZnSe:Mn is a useful electroluminescent material [6] so knowledge of its energy levels is of practical value.

2. EXPERIMENT

In order to avoid complications due to unwanted impurities, the ZnSe used in these experiments was synthesized from the elements of better than 5N purity. The concentration of zinc vacancies and of fast-diffusing impurities was reduced by treating the crystals in molten zinc. For purposes of

comparison, ZnSe ingots either with or without added manganese were grown from the vapour. Aluminium was added during growth to provide shallow donors. Dice, approximately $2 \times 2 \times 1$ mm, were cut from the ingots. Schottky diodes were made by alloying an indium ohmic contact and evaporating a gold rectifying contact. All experimental results obtained here were obtained at room temperature.

Figure 1 shows the spectrum of the short circuit photocurrent. As mentioned in the introduction, photoemission from the gold into the ZnSe accounts for a large part of the current. The threshold is about 1.4 eV : this corresponds to the barrier height and is close to the value reported by Swank et al [7]. Although the spectra for ZnSe with and without manganese differ somewhat in the region around 2.5 eV, no clear conclusion concerning manganese can be drawn from the simple photocurrent curves.

Photocapacitance spectra are shown in figure 2. There is a pronounced peak between 2.1 eV and the bandgap for material containing manganese. There is no corresponding strong feature in the material without manganese, although there is a weak feature with a threshold about 0.1 eV lower than that of the manganese peak. The sign in the change in capacity for ZnSe:Mn shows that the positive space-charge in the depletion region is being increased. It follows that the action of light is to remove electrons from the manganese to the conduction band. From the threshold of the excitation spectrum, we conclude that the filled manganese level lies roughly 2.1 eV below the conduction band.

Because the ZnSe is n-type, and because the Schottky barrier height is less than the depth of the manganese level, all the manganese levels are filled in the equilibrium state. Transitions from the valence band to the manganese levels are therefore not observed in the simple photocapacitance measurement. Suppose now that one illuminates the diode with a steady source of light of fixed wavelength, which we call the primary beam. If the primary photons have energy greater than the energy gap and can therefore produce holes,

or if they have energy greater than the depth of the manganese level and can therefore photoionize the manganese, then some proportion f of the manganese levels will be emptied. The value of f can be obtained from the steady-state rate equations but since it depends on several unknowns, e.g. the various recombination cross-sections, it is unnecessary for present purposes to write down an explicit expression for it. If a second beam of light, of variable wavelength, which we call the secondary beam, falls on the diode simultaneously with the primary beam then it can produce transitions from the valence band to the impurity, or from the impurity to the conduction band, depending on the wavelength. Figure 3 is a plot of the photocapacitance spectra obtained in this way, in which the primary beam photons have energy 2.35 eV. In ZnSe:Mn there is a threshold at about 0.65 eV at which the secondary beam can excite electrons from the valence band to those manganese levels emptied by the primary beam. The sign of the photocapacitance change confirms that the transition is transferring electrons to the manganese. Let the photoionization cross-section for transitions from the valence band to the impurity be $\sigma_v(h\nu)$, and let the concentration of impurity centres be N . Then if at some wavelength of the secondary beam the relationship

$$(1-f)N \sigma_c(h\nu) = f N \sigma_v(h\nu) \quad (1)$$

can be satisfied, then the photocapacitance change produced by the secondary beam will go through zero. Obviously the photon energy at which this occurs is not the threshold energy for transitions to the conduction band but is that at which

$$\sigma_c/\sigma_v = f(1-f)^{-1} \quad (2)$$

Since the fraction of emptied centres, f , now depends on the intensity and wavelength of both the primary beam and the secondary beam, the position of the zero will also depend on these parameters. The zero must, however, lie to the high energy side of the threshold for transitions to the conduction band. Also it is clear that if, in the vicinity of the zero, $\sigma_v f$ is small and only slowly changing while

$\sigma_c(1-f)$ is rapidly rising to a large value, then the zero will occur close to the threshold for $\sigma_c(h\nu)$. Figure 3 shows this to be the case for ZnSe:Mn and we deduce that the manganese level is about 2.0 eV below the conduction band.

3. DISCUSSION

The photocapacitance measurements described here show that in ZnSe:Mn there is an impurity level lying 2.0 eV below the conduction band and 0.65 eV above the valence band. Any possible ambiguity as to whether the level is 2.0 eV below the conduction band or 2.0 eV above the valence band has been resolved by observing the sign of the photocapacitance change. Zinc selenide prepared in a similar manner but not containing manganese gives a weaker photocapacitance signal, presumably due to stray impurities of lattice defects. We therefore conclude that the observed level is associated with manganese.

Optical absorption [8] and spin resonance [9,10] measurements show that manganese in ZnSe is normally in the d^5 configuration. A detailed investigation of the optical absorption of ZnSe:Mn by Dr E M Wray of the Department of Physics in the University of St Andrews has shown that the manganese is on an isolated substitutional site and in the d^5 configuration, whether or not the material has been treated in molten zinc. No evidence for manganese in other states or associated in complexes has been found. There is therefore good reason for believing that the level 2.0 eV below the conduction band is produced by substitutional manganese atoms, and that when the level is filled the manganese is in the d^5 configuration. To make the identification certain, one should show that the density of levels and the density of Mn d^5 centres are equal. We have not yet attempted this.

It can be seen from figure 3 that the threshold energies can be determined to within ± 0.05 eV. In order to obtain more accurate information one may use photoconductance measurements. With more accurate data, one must then take

phonon interactions into proper account in the interpretation. Work along these lines is in progress.

ACKNOWLEDGEMENTS

We thank Dr E M Wray for letting us use his unpublished data on optical absorption. J W Allen is grateful to Tullis Russell Co for a Fellowship.

REFERENCES

1. H G GRIMMEISS and M O OTTOSSON, phys stat sol (a) 5, 481 (1971)
2. G BJÖRKLUND and H G GRIMMEISS, Solid-State Electronics 14, 589 (1971)
3. A F TASCH and C T SHAH, Phys Rev B1, 800 (1970)
4. C T SAH, L L ROSIER and L FORBES, Appl Phys Letters 15, 161 (1969)
5. C T SAH, L FORBES, L L ROSIER, A F TASCH and A B TOLE, Appl Phys Letters 15, 145 (1969)
6. J W ALLEN, A W LIVINGSTONE and K TURVEY, Solid-State Electronics, to be published
7. R K SWANK, M AVEN and J Z DEVINE, J Appl Phys 40, 89 (1969)
8. D W LANGER and H J RICHTER, Phys Rev 146, 554 (1966)
9. R S TITLE, Phys Rev 131, 2503 (1963)
10. B C CAVENETT, Proc Phys Soc 84, 1 (1964)

CAPTIONS TO THE FIGURES

- Figure 1 Short-circuit photocurrent spectrum of a Schottky diode of ZnSe with and without manganese.
- Figure 2 The change of capacitance on illumination of a ZnSe Schottky diode. - ZnSe with manganese, --- ZnSe without manganese.
- Figure 3 The change of capacitance of a ZnSe Schottky diode produced by a secondary light source, with a constant primary light source of photon energy 2.35 eV. - ZnSe with manganese, --- ZnSe without manganese.

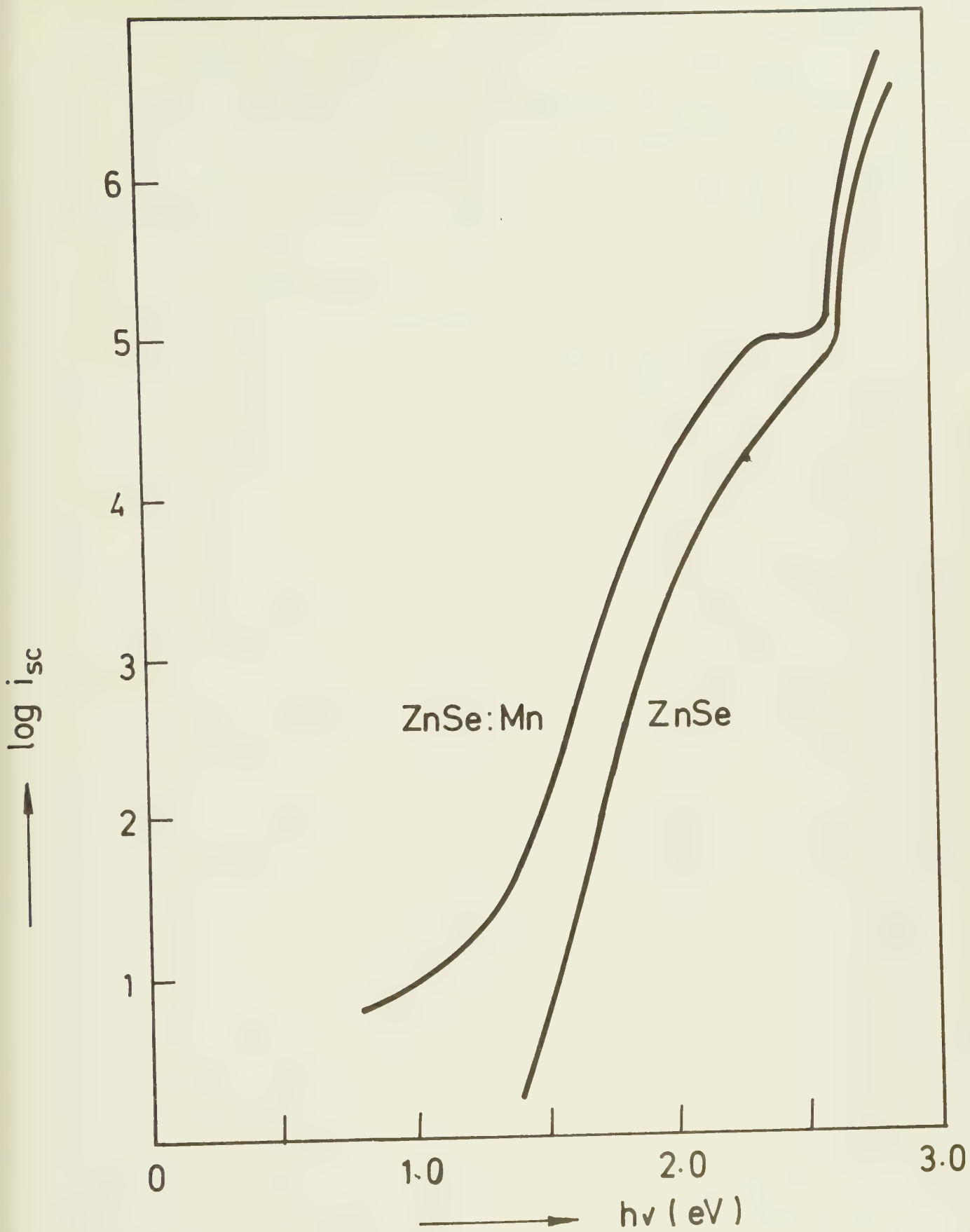


Fig 1

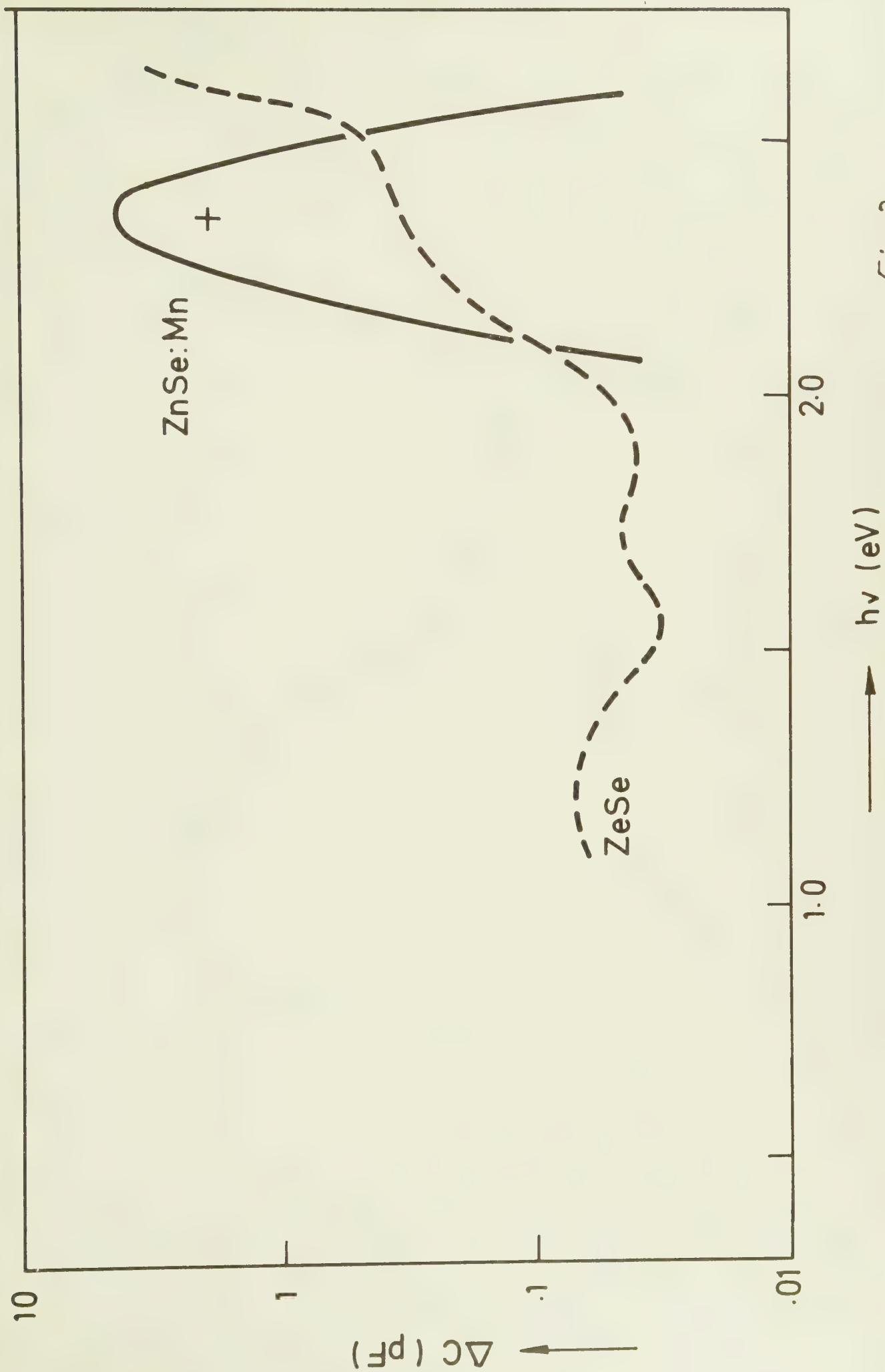


Fig 2

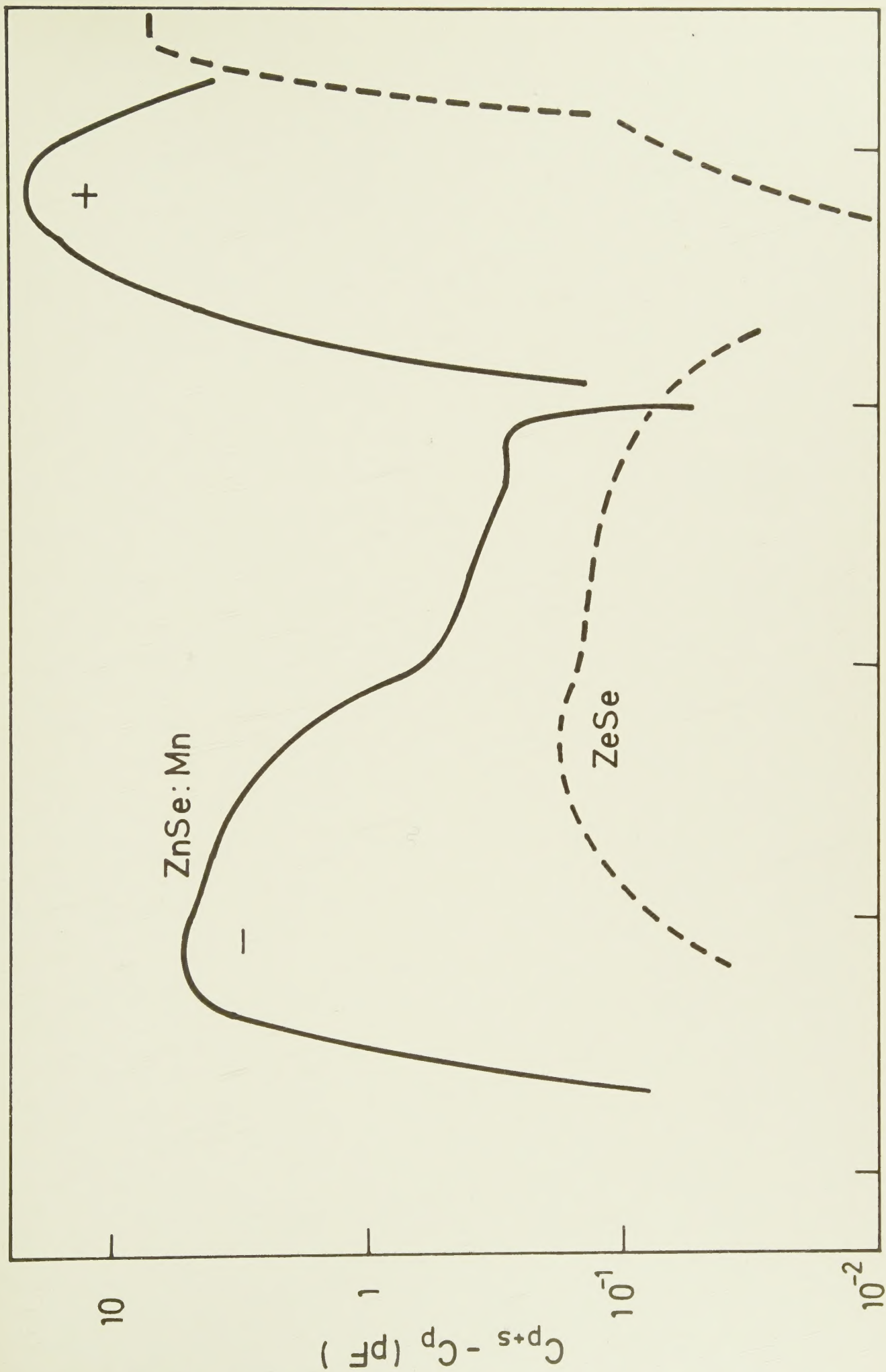


Fig 3

